STUDIES IN TRANSITION METAL COORDINATION CHEMISTRY

PART I: MODEL STUDIES OF MOLYBDENUM(V) AND (VI) COMPLEXES

PART II: CRYSTALLOGRAPHIC STUDIES OF MOLYBDENUM COMPLEXES

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ABBREVIATIONS

acac - pentane-2,4-dione

AcBr - acetylbromide

AcCl - acetylchloride

Ac_2O - acetic anhydride

asp - aspartato ion

bipy - α,α'-bipyridyl

dien - diethylenetriamine

diphosphine - bis-1,2-(diphenylphosphino)ethane

diphosphinedioxide - bis-1,2-(diphenylphosphineoxide)ethane

DMA - dimethylacetamide

DMF - dimethylformamide

DMSO - dimethylsulphoxide

dtc - diethyldithiocarbamate

EDTA - ethylenediamine-N,N,N',N'-tetraacetic acid

FAD - flavinadeninedinucleotide

FMN - flavinmononucleotide

IDA - iminodiacetic acid

kK - kilokausers

L - ligand molecule

Me_3AsO - trimethylarsineoxide

Me_3NO - trimethylamineoxide

MIDA - N-methyliminodiacetic acid

NTA - nitrilotriacetic acid

ophen - o-phenanthroline

O_t - terminal oxygen atom attached to a metal centre

oxine - 8-quinolinol

Ph_3AsO - triphenylarsineoxide

Ph_3P - triphenylphosphine

Ph_3PO - triphenylphosphineoxide

pyNO - pyridine-N-oxine

THF - tetrahydrofuran

UDA - uramil-N,N-diacetic acid

xanthate - ethylxanthate

δ - infrared bending mode of vibration

ν - infrared stretching mode of vibration

ν^s, ν^a - symmetric and asymmetric modes

μ - magnetic moment (in Bohr Magnetons)

μ_{s-o} - spin-orbit magnetic moment

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MODEL STUDIES OF MOLYBDENUM(V) AND (VI) COMPLEXES

CHAPTER 1

INTRODUCTION

The work in this thesis was aimed at elucidating aspects of the coordination chemistry of molybdenum in the +5 and +6 oxidation states which are related to the function of molybdenum in biological systems. This work is divided into two sections. Part I (chapters 1 to 5) is concerned with the preparation, characterisation and infrared studies of molybdenum (V) and (VI) complexes. Part II (chapters 6 to 9) involves crystallographic studies made on selected compounds including full structure analyses of three molybdenum complexes.

In chapter 2 the current state of the literature, as regarding molybdenum coordination chemistry and the involvement of molybdenum in biological systems, is summarised. Chapter 3 is concerned with studies made on model compounds. Molybdenum (V) and (VI) complexes were synthesised, characterised and studied using physical inorganic techniques. One section deals with a detailed study of infrared spectra of $MoO_2X_2L_2$ adducts (X = Cl, Br; L = monodentate aprotic ligands) including assignments of all vibrational modes down to 100 cm^{-1}.

The preparation and characterisation of molybdenum complexes with ligands of biological interest is presented in chapter 4. Several new complexes of molybdenum (V) and (VI) with synthetic and naturally occurring aminoacids were synthesised and characterised. Part I of the thesis is completed with chapter 5 which describes the experimental work carried out.

In part II, chapter 6 deals with those methods and techniques which are used in the University of Canterbury Crystallographic Laboratory during the process of structure determination. Results are presented for preliminary studies made on compounds which were not subsequently further investigated. Chapter 7 presents the results of a structure analysis on the complex cis-dioxobis(butane-2,3-diolato)-molybdenum(VI)bis(butane-2,3-diol). In this structure it is shown that the chelate rings are nearly planar. Also the solvate molecules are attached to the central moiety and linked to one another by a system of hydrogen bonds which extends throughout the crystal.

A new metal oxo system for molybdenum (V) is reported in chapter 8 which describes the structure analysis of the compound ammonium cis-dioxouramil-N,N-diacetatomolybdenum(V)-monohydrate. This compound is found to contain a monomoic cis-dioxo group, the first such to be structurally characterised for molybdenum(V). Further it is found that the two glycinato rings of the ligand are attached to the molybdenum atom in the stereochemically more unfavourable trans arrangement. Chapter 9 describes the crystal structure of the compound tripotassium cis-trioxonitrilotriacetatomolybdenum-(VI)monohydrate. This compound is shown to contain a cis-trioxo grouping and has the ligand in an arrangement in which the two glycinato groups are attached to the molybdenum atom in a cis arrangement. The molybdenum is not seven-coordinate as has been suggested[1]; rather the third glycinato group is unattached to the molybdenum and contains an anionic carboxylato group.

CHAPTER 2

2.1 THE COORDINATION CHEMISTRY OF MOLYBDENUM (V) AND (VI)

2.1.1 Introduction

The chemistry of molybdenum in the +6 and +5 oxidation states is dominated by the existence of a wide variety of oxo species of the type $Mo_x O_y^{n+}$, with one or more oxygen atoms as terminal or bridging ligands[2]. This situation stems from the fact that the molybdenum oxygen multiple bond is extremely stable and persists throughout a wide range of compounds and reactions. The oxo species obtained depends on the pH of the solution from which the complex or compound is isolated and on the requirements of the ligand. The following oxo species have been characterised by structural studies:

Mo VI; MoO^{4+}[3], MoO_2^{2+}[4], $Mo_2O_5^{2+}$[5], MoO_3[6], MoO_4^{2-}[7].

Mo V ; MoO^{3+}[8], $Mo_2O_3^{4+}$[9], $Mo_2O_4^{2+}$[10].

In the literature there appears to be no reference to any molybdenum (V) compound in which the metal is bonded to more than one terminal oxygen atom[2,11]. Molybdenum forms a wide range of complexes with inorganic donors[2,12]. Oxo species of molybdenum behave essentially as class (a)[13] acceptors but do form extremely stable complexes with organic ligands containing thiol groups. It is this versatility in the coordination behaviour of molybdenum which makes its chemistry so interesting.

A number of X-ray crystal structures have been reported (see next section) and these serve to illustrate the

structural peculiarities that may develop within this general class of compounds. They may be best illustrated by the case of the molybdenum (VI) malate compound, which had been formulated as $(NH_4)_2[(MoO_3)_2C_4H_4O_5]2.5H_2O$. However a complete determination of the structure revealed the actual formula to be $(NH_4)_4[Mo_4O_{11}(C_4H_3O_5)_2].6H_2O$, with exactly the same ratio of atoms but a completely different coordination environment for the molybdenum atoms[14].

The aqueous solution chemistry of molybdenum (V) has been studied mainly by spectroscopic and magnetic measurements. In a very strongly acid environment the species found appears to be $MoOX_5^{2-}$ ($HX \geq 10M$, X = Cl,Br). Increasing the pH of the solution leads to dimerization with successively one, then two oxygen bridging atoms[15]. The solution chemistry of molybdenum (VI) is complicated by the extensive interconversions which occur among polymeric species except in strongly basic or acidic solutions where MoO_4^{2-} and MoO_2^{2+} respectively predominate. The sequence of reactions appears to be[16,17]:

$$[MoO_4]^{2-} \xrightarrow{pH\ 6} [Mo_7O_{24}]^{6-} \xrightarrow{pH\ 3} [Mo_8O_{26}]^{4-} \xrightarrow{pH < 0} MoO_2^{2+}$$

2.1.2 Structural Studies on Molybdenum (V) and (VI) Complexes

A large number of crystal structures has now been reported for molybdenum (V) and (VI) compounds (see appendix A for details of bond lengths and references) and trends can be noted. With only two exceptions, in each of these structures the molybdenum atom is found to be in a distorted octahedral environment. The exceptions arise with molybdenum (V) complexes with cysteine esters where the molybdenum atoms are found to be in a distorted trigonal bipyramidal environment[18,19].

In these particular cases the reason proposed for the sixth position not being filled in the molybdenum coordination sphere is the severe steric interactions that would result between the ether groups if the ethereal oxygen atoms were to complete the sixfold coordination. The molybdenum ethereal oxygen bond is not strong enough to overcome these repulsions[19].

The more significant facts which emerge from a study of the bond lengths and angles in these compounds are that bonds from molybdenum to terminal oxygen atoms exhibit considerable multiple bond character, and range in length from 1.60[20] to 1.86Å [21] in both molybdenum (V) and (VI) compounds whilst angles between terminal oxygen atoms are always greater than 100° due to the repulsions of the terminal oxygen atoms (a direct result of their being much closer to the molybdenum than any other type of atom). Bonds between molybdenum and bridging oxygen atoms range from 1.86 [9] to 1.95Å [10]. However in some cases there is considerable asymmetry in the Mo $\underline{(1)}$ O $\underline{(2)}$ Mo bridge although the mean of the Mo $\underline{(1)}$ O, Mo $\underline{(2)}$ O lengths lies in the stated range[10,22,23,24]. Bond lengths to other types of atoms depend on the particular position that the atom occupies in the coordination sphere. The range of lengths for a molybdenum oxygen (ligand) bond is 1.91 [25] to 2.34Å [26], for molybdenum nitrogen is 2.23 [19] to 2.45Å [27], for molybdenum sulphur is 2.18 [28] to 2.70Å [9], for molybdenum water is 2.22 [29] to 2.45Å [30], for molybdenum fluorine is 1.86 [31] to 2.11Å [32], for molybdenum bromide is 2.52 [35] to 2.83Å [21]. Using Cotton and Wing's[36] relationship between molybdenum oxygen bond lengths and molybdenum oxygen bond orders, the three types of molybdenum oxygen bond correspond to bond orders of 3.0 to 1.5, 1.5 to 1.25, 1.25 to

0.8 for terminal, bridging and ligand bonds respectively. The fact that water forms a very weak bond to molybdenum is illustrated by the maximum bond order of the molybdenum oxygen (water) bond of 0.8.

Those bonds between molybdenum and ligand atoms which are trans to multiple molybdenum oxygen bonds are significantly longer than normal because of the competition for the available molybdenum 4d orbitals for π bonding. This can be seen in all molybdenum (V) and (VI) structures containing terminal oxygen atoms and the molybdenum (V) xanthate complex affords a good example of this effect[9]. In this complex there are three distinct types of molybdenum sulphur bond. The longest is that trans to a terminal oxygen bond (2.70Å). The bond trans to a bridging oxygen atom is 2.53Å whilst that trans to another sulphur atom is 2.46Å.

2.1.3 Stereochemistry of Molybdenum V and VI Complexes

An analysis of experimental data, mainly from X-ray structure determinations and infrared results, leads to the conclusion that the stereochemistry of molybdenum oxo compounds has two major characteristics. The first is the tendency of molybdenum to distorted octahedral coordination with distortions that are completely predictable[37]. In compounds of molybdenum (V) and (VI) the multiply bonded oxygen atoms always significantly weaken the bond from molybdenum to the trans ligands. This phenomenon is revealed by a significant increase in the length of this bond.

The second characteristic of molybdenum stereochemistry is that in di- and trioxo compounds the terminal oxygen atoms are always located in a mutually cis grouping[37]. Although

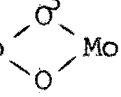
prior to this work there were no authenticated reports of a molybdenum (V) oxo complex with a monomeric dioxo[11] or trioxo grouping, suggestions had been made that such groupings might have a cis arrangement[37].

Some workers have, on the basis of infrared and other experimental studies, predicted trans dioxo groupings for molybdenum (VI) complexes, e.g. the complexes: $M_2MoO_2Cl_4$, M = K,Rb,Cs[38,39] and $MoO_2Cl_2$2dimethylformamide, $MoO_2Cl_2$2DMA, $MoO_2$2acac, and $MoO_2$2oxinate[40]. However, these predictions have been shown to be incorrect by subsequent X-ray molecular structure analyses[41-44].

As has been mentioned in 2.1.2, two structures have been reported of five coordinate molybdenum (V) complexes[18,36]. In both cases the cysteine ester complexes were recrystallised from acetonitrile without the sixth position being occupied. Steric factors have been proposed as the explanation for this unusual coordination environment.

The reported structures of the ions $[MoOF_5]^{2-}$[31], $[MoOCl_5]^{2-}$[21] and $[MoOBr_5]^{2-}$[21] also show the effect on the other ligands of the multiple oxygen bond. The respective bond lengths for halide trans to oxygen and cis to oxygen are 2.02, 1.88; 2.63, 2.40 and 2.83, 2.56Å. These observations illustrate the general tendency in molybdenum (V) and (VI) complexes to concentrate the π bonding in bonds formed with the oxygen atoms at the expense of the bonds formed with other ligands[21] in a mixed complex.

2.1.4 The Molybdenum Oxygen Bonding Interaction

The molybdenum oxygen bonding interaction has been treated by a number of workers[37,45-52]. One of the reasons proposed for the importance of metal oxo bonding in molybdenum (V) and (VI) compounds is that molybdenum has both σ bonding and π antibonding subshells empty and is therefore ideally suited to accommodate strongly nucleophilic oxide π electrons. This discussion will be limited to oxygen atoms which are either terminally bound to molybdenum; e.g. MoO, MoO_2 and MoO_3, or are bridging molybdenum atoms, e.g. Mo - O - Mo and  .

The first case to consider is that of the Mo - O group as found in such compounds as $[MoOCl_5]^{2-}$ [45]. A molecular orbital treatment was proposed for the vanadyl ion VO^{2+} [46] and adapted to the isoelectronic MoO^{3+} ion by the same workers[45] (see figure 2.1). Whilst the authors considered the influence of all ligands, the molecular field is dominated by the axial metal oxygen interaction. The resulting model had a triple Mo - O bond made up of one strong σ bond and 2 π bonds. The strength of this triple bond is indicated by the metal oxygen stretching frequency which is found in the vicinity of 1000 cm^{-1} for both molybdenum (V) and (VI) compounds[53,54].

The second case to consider is that of the dioxo groups MoO_2^+ and MoO_2^{2+}. A model for these groups has been proposed[47] based on earlier treatments[45,46,48]. The model assumes overlap of oxygen 2p orbitals with suitably oriented metal d orbitals. Only $p\pi - d\pi$ overlap is considered since use of metal s and p orbitals does not affect symmetry considerations. (The energy difference between 5s and 5p orbitals and 4d orbitals would also prevent adequate mixing of orbitals.) A bonding scheme can be drawn up (figure 2.2) in which it can be seen that in

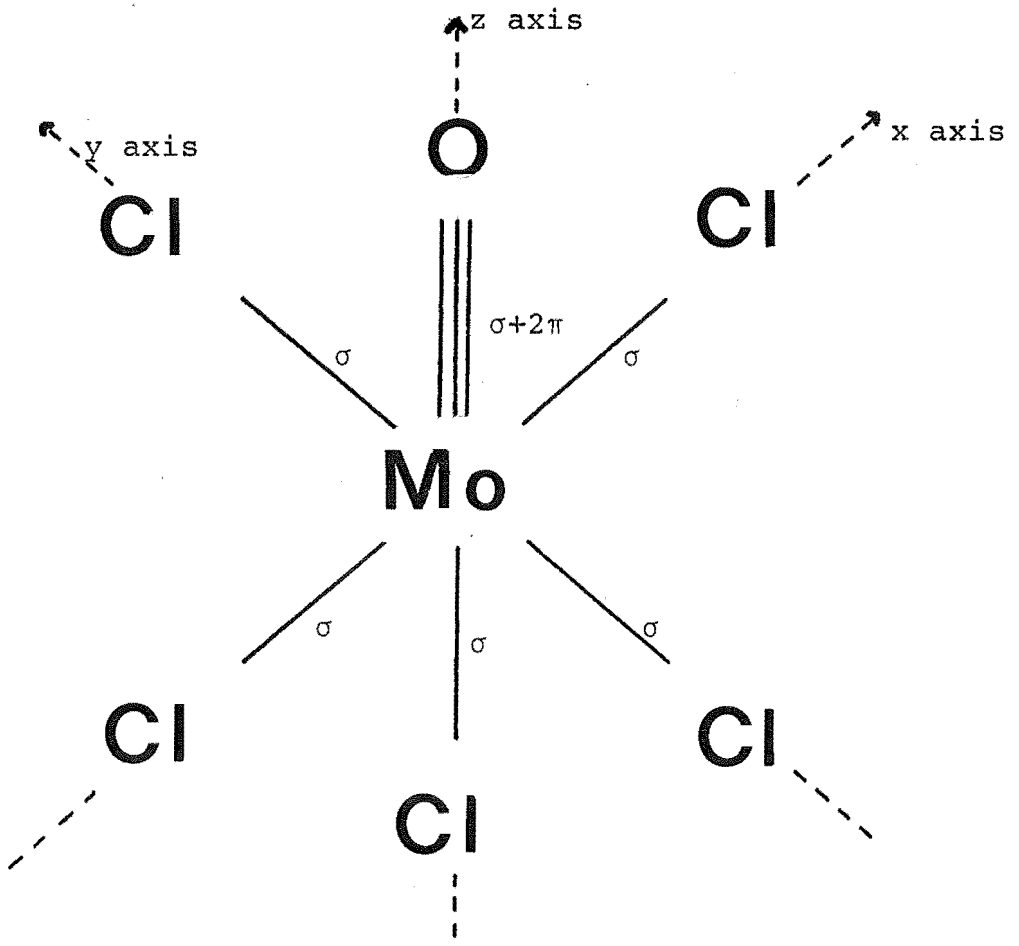


Fig. 2.1(a) Structure of the $[MoOCl_5]^{2-}$ ion.

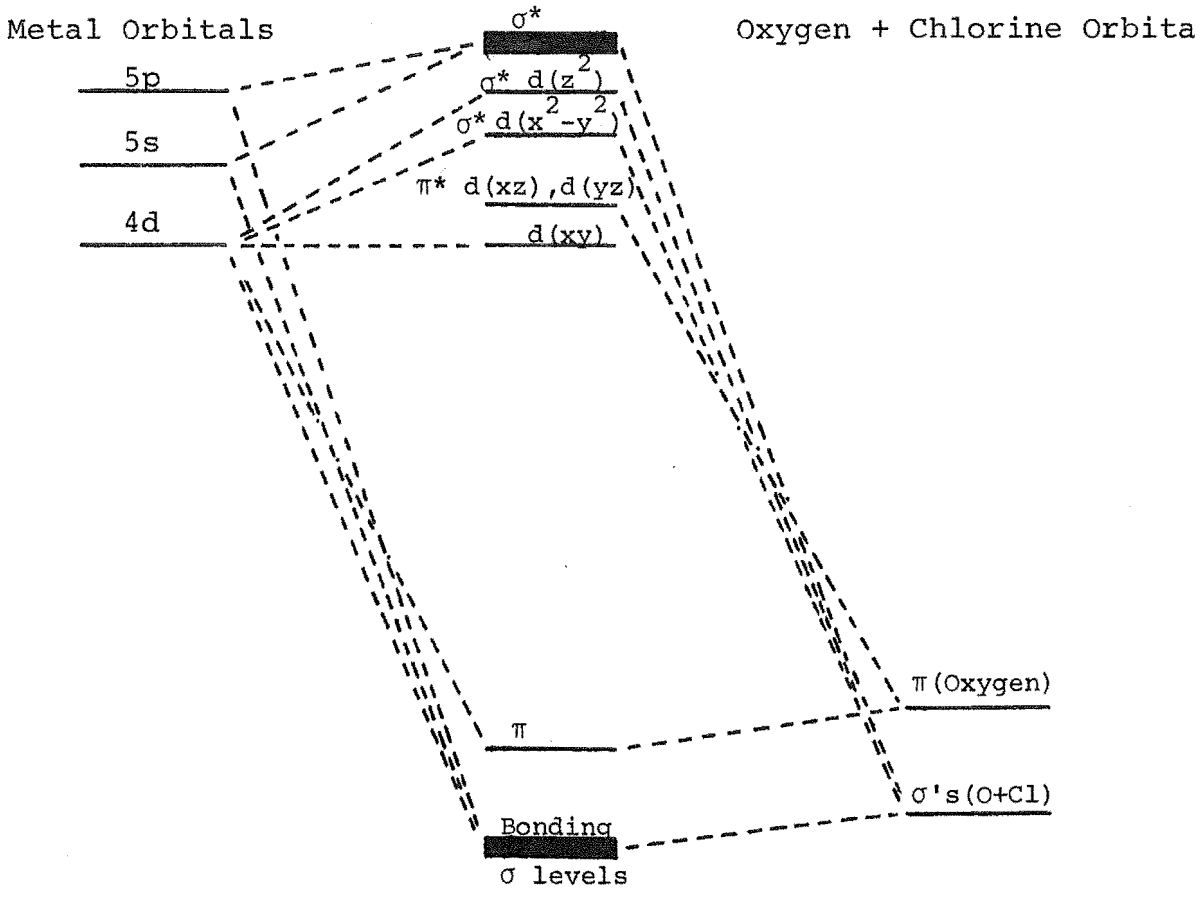
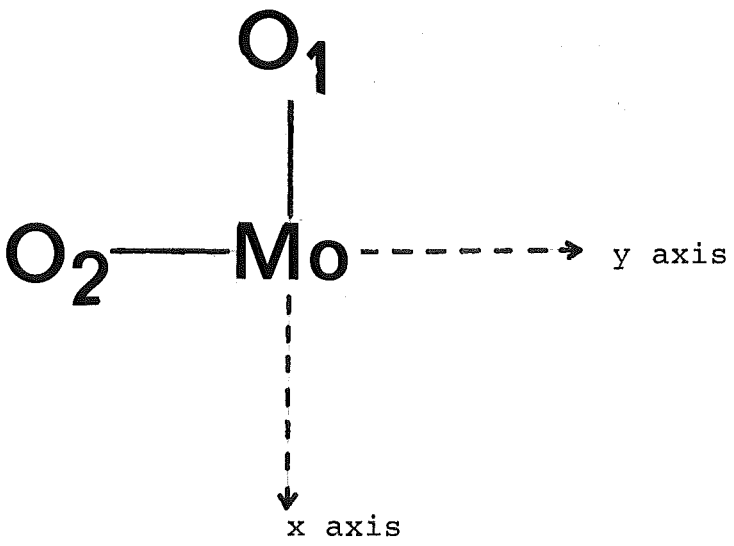
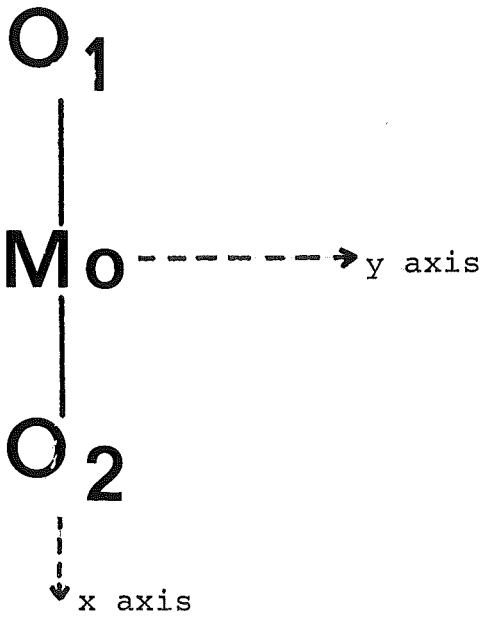


Fig. 2.1(b) Molecular Orbital Scheme for the $[MoOCl_5]^{2-}$ Ion



O_1 overlap	O_2 overlap
$2p_y - d_{xy}$	$2p_x - d_{xy}$
$2p_z - d_{xz}$	$2p_z - d_{yz}$

Fig. 2.2(a) Orbital overlap for a Cis-Dioxo System



O_1 Overlap	O_2 Overlap
$2p_y - d_{xy}$	$2p_y - d_{xy}$
$2p_z - d_{xz}$	$2p_z - d_{xz}$

Nonbonding orbital d_{yz}

Fig. 2.2(a) Orbital overlap for a Trans-Dioxo System

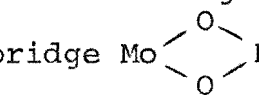
the cis dioxo case each oxygen atom has exclusive use of one of the metal t_{2g} orbitals and shares a third, whilst for the trans configuration the model has both oxygen atoms sharing two t_{2g} orbitals leaving one nonbonding t_{2g} orbital.

It is thus expected that for d^o metal ions the oxygen atoms should adopt a cis configuration giving better overlap and thus strong metal oxygen bonds. The cis arrangement for d^o metal ions has been well established for the case of molybdenum[37]. These predictions have also been borne out for other d^o metal ions. In recent papers[55-58] the structures of some vanadium (V) dioxo complexes have been reported showing that the cis configuration is also adopted by V^{5+} (d^o). These compounds also show the same trans effects (lengthening of the bonds trans to $V-O_t$) as in the corresponding molybdenum(VI) compound. Thus the predictions made regarding d^o metal ion oxo species[37] appear to be applicable to all transition metal ions having this configuration.

For d^2 metal ions a trans arrangement should be favoured allowing the two d electrons to be located in a nonbonding t_{2g} orbital. This prediction has been confirmed by structure analyses on dioxo species with d^2 metal ions, e.g. Mo^{IV} [59], Re^{V} [60], Os^{VI} [61]. For a MoO_2^+ grouping with only one unpaired electron two cases may arise[37]. The unpaired electron may occupy either one of the three t_{2g} nonbonding orbitals, which would then exclude this orbital from π-acceptor interactions with the oxygen atoms, or one of the antibonding $4d\sigma^*$ orbitals leaving all three nonbonding σ orbitals to the π electrons from the oxygen atoms. In the first case a trans dioxo grouping would result and in the second case a cis grouping would

arise. Prior to this study, no MoO_2^+ grouping had been characterised[11].

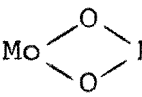
A third type of molybdenum oxygen grouping encountered is in trioxo MoO_3 complexes. No molybdenum (V) trioxo group has been reported. For the molybdenum (VI) case a cis arrangement allows equal sharing of the metal t_{2g} orbitals and for this reason is preferred over the trans grouping. This configuration[1,6] is observed in compounds such as MoO_3dien and $[(MoO_3)_2EDTA]^{4-}$.

Oxygen bridging between metal centres also is important in molybdenum (V) and (VI) compounds. Two types of bridge can occur, either a single oxygen bridge Mo - O - Mo, or a double oxygen bridge  . The electronic structures of these groupings are most conveniently described by the molecular orbital method. The single oxygen bridge will be considered first. Models for the electronic structure of this core have been proposed[49,50] in which the Mo - O - Mo group was treated as an isolated species and only the interactions between bridging oxygen and acceptor atoms were taken into account. However, it was found that omission of the interactions of the five other ligands of a local distorted symmetry (and hence increased mixing of atomic orbitals) resulted in serious deficiencies in the model[51,52].

A full treatment of the M - O - M group including contributions from other ligands in a mixed ligand complex has therefore been developed[51]. Three types of interaction need consideration. Firstly the interactions between the oxygen bridge and both metal nuclei in the MOM core. Secondly, the interaction between the metal ions and their local ligand environments need to be included. Lastly the interactions

between ligands placed in the xy planes perpendicular to the bridge axes need consideration. The two latter interactions affect the electronic structure of the core and hence its related physical properties, and therefore must be included in any analysis which explains such properties.

The calculations carried out[51] result in a set of molecular orbitals composed of the p orbitals of the bridging oxygen atom, the d orbitals of the metal ions, and the π orbitals (of appropriate symmetry) of the other ligands. The bridging molecular orbitals are characterised by considerable electron delocalization caused by the large overlap and similar energies of the orbitals involved. The electrons for these bridging molecular orbitals come from the oxygen atoms (fig. 2.3). The other molecular orbital in this scheme is essentially a nonbonding orbital. The metal d electrons are placed in this orbital. Thus the oxygen bonding makes possible the pairing of electrons placed in the one molecular orbital but arising from both metal atoms.

Comparison between systems with double oxygen bridging and single oxygen bridging suggests that the presence of two bridging oxygen atoms, and also such strong π bonding ligands as terminal oxygen atoms, results in a weakening of the bridge π bonds and hence a lowering of the multiplicity of the bridge bond. The difference can be seen in the lengths of the Mo - O bond in Mo - O - Mo and  at 1.85Å (average) and 1.95Å (average) respectively (see Appendix A). There is then an increase in the importance of metal oxygen σ interactions in holding the bridge together[51]. Due to the decrease in the molybdenum molybdenum distance a direct metal metal interaction appears as shown by a lowering of the magnetic moment and

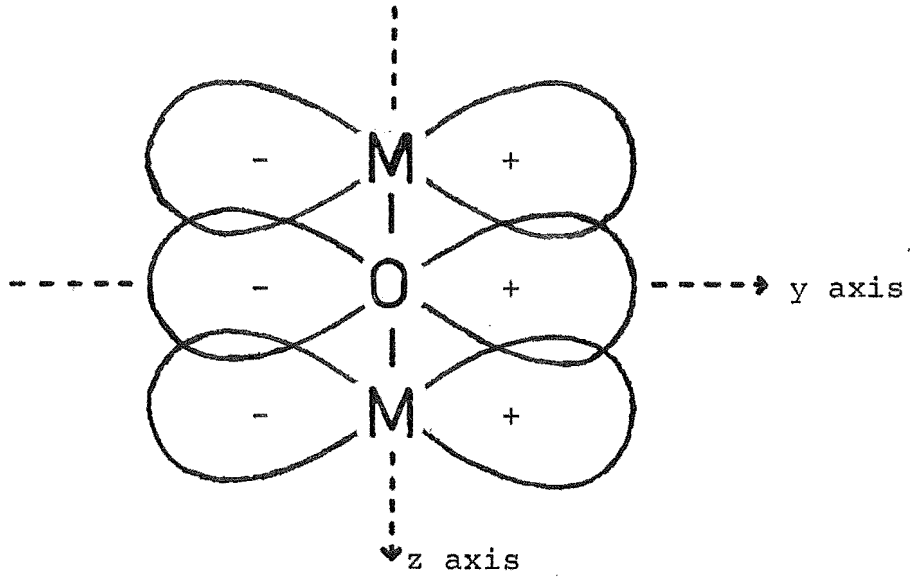


Fig. 2.3(a) Overlap of Metal d_{yz} with Oxygen p_y Orbitals

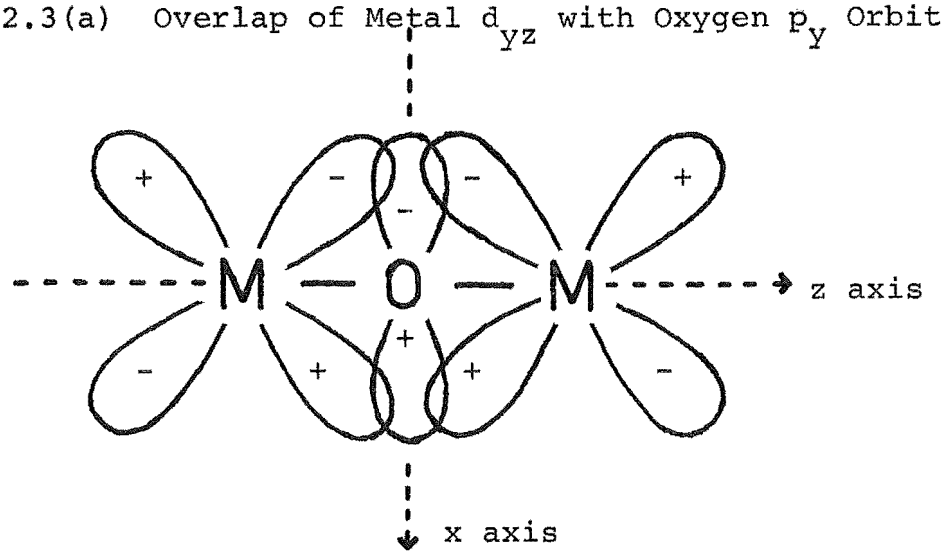


Fig. 2.3(b) Overlap of Metal d_{xz} with Oxygen p_x Orbitals

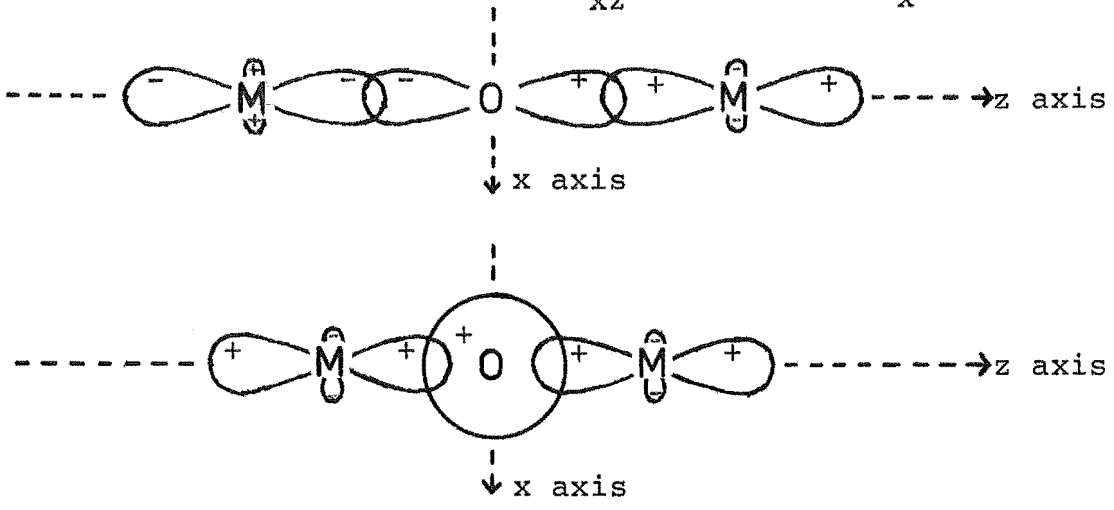


Fig. 2.3(c) Overlap of s and p_z orbitals of oxygen and the d_z2 orbitals of the metal atoms.

change in the u.v. and visible absorption spectrum.

The molecular orbital scheme proposed for this system[51] involves combinations of the $d(z^2)$ and $d(x^2-y^2)$ orbitals forming the σ bonds along the x, y and z axes, while the other d orbitals contribute to the molecular π bonds. Because of the short metal metal distance, a σ Mo - Mo interaction through the dxy orbitals is possible (fig. 2.4).

2.1.5 Infrared Spectra of Molybdenum (V) and (VI) Compounds

As the chemistry of molybdenum (V) and (VI) coordination complexes is dominated by the metal oxygen interaction, so the infrared spectra of these complexes are most easily characterized in terms of the molybdenum oxygen bonding interaction. Values for molybdenum oxygen stretching frequencies are reported in Appendix B. Values for the molybdenum terminal oxygen stretching frequency are in the range 850-1000 cm^{-1}, the actual value depending on the nature of the oxo species, the oxidation state of the molybdenum and the nature of the other ligands[2].

For molybdenum (VI) compounds the metal terminal oxygen stretching frequencies ($\nu(M_o-O_t)$) tend to decrease in the order:

$$MoO^{4+} > MoO_2^{2+} > MoO_3;$$

and similarly for molybdenum V compounds:

$$MoO^{3+} > Mo_2O_3^{4+} > Mo_2O_4^{2+}.$$

These trends can be correlated with the expected decrease in π bonding in these species (see section 2.1.4).

A consideration of the symmetry properties of the various oxo groupings enables predictions to be made regarding the number of infrared active modes to be expected in these

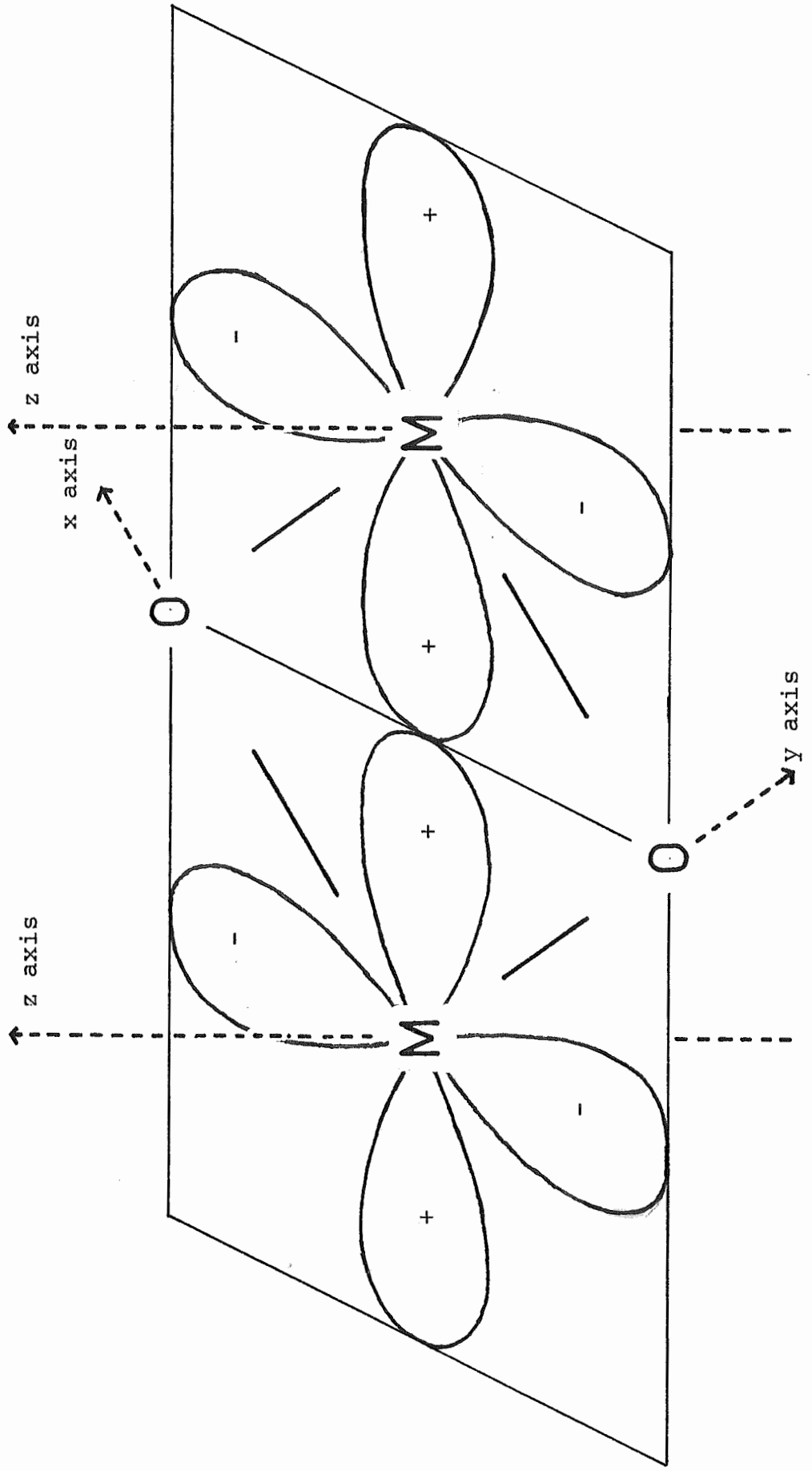


Fig. 2.4 Possible Overlap of d_{xy} Orbitals for a σ M-M Bond.

compounds. For cis trioxo groups of point group symmetry C_{3v} four modes are expected ($2A_1 + 2E$), all infrared active. Three bands are observed, two in the region 800-900 cm^{-1} and one ca. 300 cm^{-1}. These may be designated as the symmetric stretch (A_1 symmetry), the asymmetric stretch (E symmetry) and a deformation mode ($A_1 + E$)[47]. Overlapping of deformation modes has also been observed in vanadate species[62]. In some MoO_3 compounds only one band is found in the 800-900 cm^{-1} region. This is ascribed to the accidental degeneracy of the symmetric and asymmetric modes[63].

It has been found[36] that in order to interpret the spectra of molecules having two or more terminal oxygen atoms connected to a common metal atom it is necessary to consider the manner in which the vibration of one metal oxygen bond interacts with the vibrations in the others. This interaction is via metal-oxygen π bonding and can be attributed to the overlap of filled $p\pi$ orbitals on the oxygen atom with empty $d\pi$ orbitals on the metal. Each of the d orbitals will be available to two or more of the oxygen atoms. The coupling of vibrations should be most noticeable in metal ions having a d^o configuration as then the maximum number of d orbitals is available for $p\pi - d\pi$ interactions with the oxygen atoms. This in part explains the importance of metal oxygen bonding in molybdenum (VI) (d^o) and molybdenum (V) (d^1) chemistry.

In a cis grouping of terminal oxygen atoms as one metal oxygen bond stretches lessening the involvement of some of the $d\pi$ orbitals in the π bonding to that atom, these same orbitals become more available for π bonding to the other oxygen atoms strengthening their bonds to the metal ion. The stretch-stretch

interaction constants should thus be positive for this type of grouping.

For a cis dioxo compound of point group symmetry C_{2v}, three vibrational modes are expected[47] of symmetry species $2A_1 + B_2$, all active in the infrared spectrum. Two bands occurring in the region 900-960 cm^{-1} have been assigned to ν^a (Mo - O_t) (B_2) and ν^s(Mo - O_t) (A_1) respectively ($\nu^a < \nu^s$). A band occurring in the vicinity of 380 cm^{-1} has been assigned to a deformation mode $\delta(MoO_2)$ (A_1) for this grouping[47].

For a single terminal oxygen atom only one band is predicted and this is found in the range 950-1030 cm^{-1}.

Another type of molybdenum oxygen bond is that found in oxygen bridged structures. Vibrational spectra make it possible to draw decisive conclusions about the bridge structure for single and double oxygen bridged systems[51]. For a single oxygen bridge there is a choice between linear and angular structures and by using infrared spectroscopy it is possible to give a qualitative prediction as to the bond order and bond strength and hence the π interactions between the bridge oxygen and metal ions.

The linear and angular structures differ in the number of infrared active modes found. For a linear bridge of point group symmetry $D_{\infty h}$ there will be two infrared active modes; one ν(MOM) in the region 750-900 cm^{-1} and one δ(MOM) in the region 50-150 cm^{-1}. For a bent bridge of point group symmetry C_{2v} all three modes will be infrared active; ν^s(MOM) in the region 400-600 cm^{-1}, ν^a (MOM) in the region 750-900 cm^{-1} and δ(MOM) in the region 100-220 cm^{-1}.

Dimers with two oxygen bridges can be treated as a tetra-atomic system of point group symmetry D_{2h} with six vibrational

modes of which three are infrared active. Two strong bands corresponding to the stretching frequencies of the double bridge lie in the range 450-670 cm^{-1} and 560-830 cm^{-1}.

The effect of change in angle of the MOM system on the vibrational frequencies of mono and dioxo-bridged structures has been predicted[64]. The MOM angle in a monobridged system has never been found to be less than 115°. A graph can be drawn (fig. 2.5) showing that ν^a (MOM) will be at least 215 cm^{-1} greater than ν^s(MOM). Dioxo-bridged systems, which have MOM angles in the range 80-90°, have their stretching frequencies over a much narrower range and at lower frequencies.

There are, in the literature, a number of anomalies regarding the infrared assignments of molybdenum (V) and (VI) oxygen stretching frequencies. In a recent paper[65], a seven coordinate structure was proposed for molybdenum (VI) complexes of dialkyldithiocarbamates in which a di-μ-oxo bridge was postulated. However, an examination of the published infrared spectrogram reveals no bands in the 500-900 cm^{-1} region which can be assigned to the Mo$\begin{smallmatrix} & O & \\ O & & \end{smallmatrix}$Mo system. Thus the proposed structure is in doubt. In the published spectrogram of the molybdenum (V) ethylxanthate complex[36] there is a very strong band at 946 cm^{-1} which appears to be a more reasonable assignment of $\nu(Mo-O_t)$ than the shoulder at 1046 cm^{-1}. A seven coordinate structure has been proposed for a molybdenum (V) compound of diarsine[66] in which a bridging oxygen atom was postulated on the basis of a "low" $\nu(Mo-O_t)$ value of 956 cm^{-1}. However values of $\nu(Mo-O_t)$ for $MoOCl_3.2L$ complexes, of 940 cm^{-1} have been well authenticated[67]. A six coordinate structure appears to be more likely.

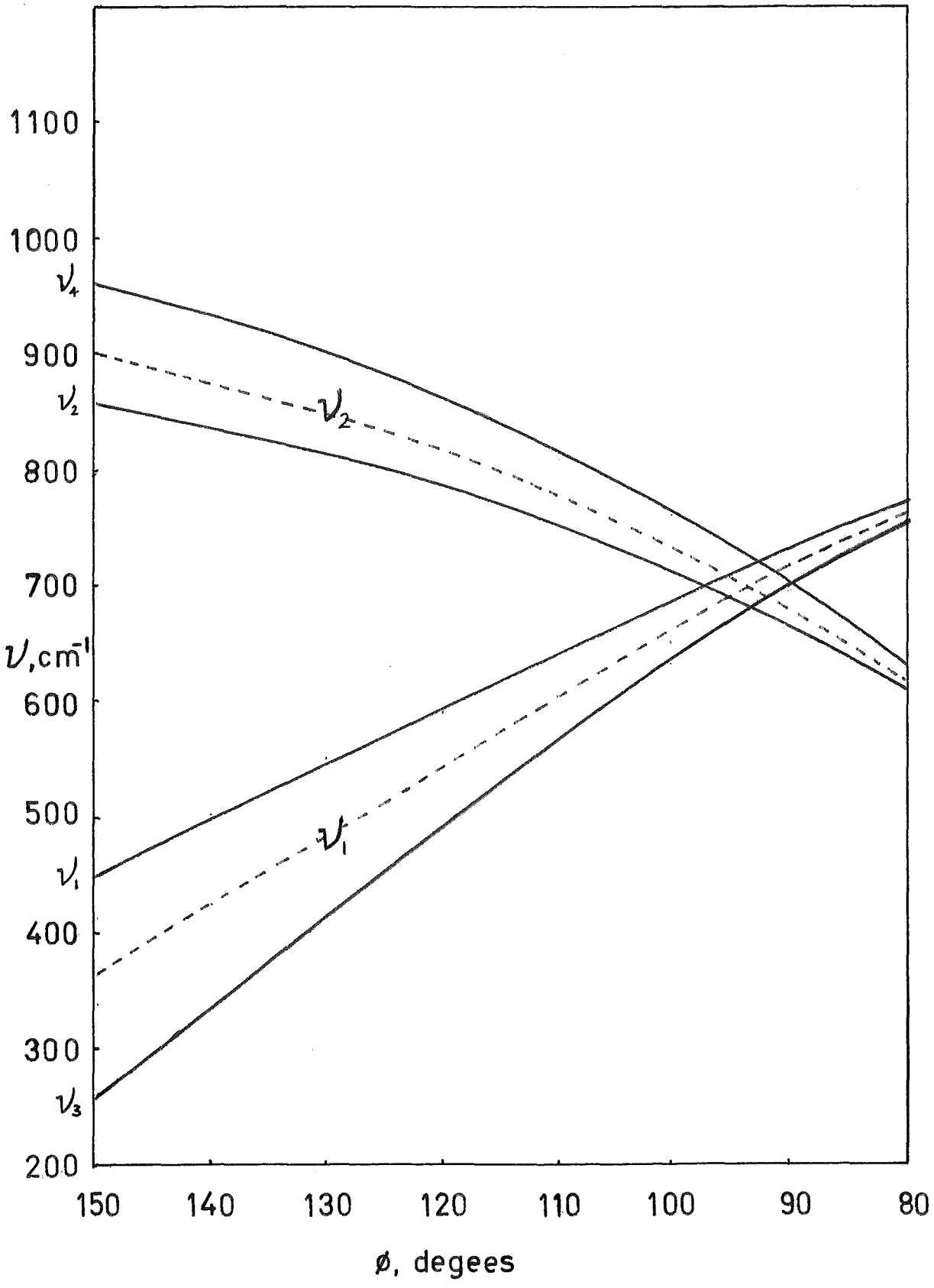


Fig. 2.5 Variation in Metal Oxygen Bridge Vibrations as a Function of the MOM angle.

The change in infrared frequency with change in oxidation state, for a similar coordination environment, appears to be slight; for $MoOCl_3$ $\nu(Mo-O_t)$ is found at 1020 cm^{-1} [68], for $[MoOCl_4]^-$ [69] at 1000 cm^{-1} and for $MoOCl_4$ [40] at 997 cm^{-1}. The molybdenum oxygen frequency is more sensitive to changes in the nature of the ligands.

A number of assignments have been made for molybdenum (V) and (VI) halogen stretching frequencies. This is because of the relative ease of assignment of these frequencies due to the mass effect. From the available data it appears that $\nu(Mo-F)$ occurs in the range 450-550 cm^{-1}, $\nu(Mo-Cl)$ in the range 300-350 cm^{-1} and $\nu(Mo-Br)$ in the range 200-250 cm^{-1}. A small number of assignments have been made of molybdenum ligand stretching frequencies for oxygen, nitrogen and sulphur donors (see chapter 3).

2.1.6 U.V. and Visible Spectra of Molybdenum (V) and (VI) Complexes

Most papers which report the preparation of molybdenum (V) and (VI) complexes also report the positions (and sometimes absorbance) of peaks in their ultraviolet and visible spectra (see appendix C). However, only a few authors have attempted to provide models on which assignments can be based.

The first such model, and the one on which all subsequent studies have been based, was proposed by Gray and Hare in 1962[45]. In this paper the electronic spectrum of the $[MoOCl_5]^{2-}$ ion was interpreted on the basis of an ion of C_{4v} symmetry with a short molybdenum oxygen bond. The molecular orbital scheme used is shown in figure 2.2b. The π bond from the oxygen atom makes the molybdenum (dxz, dyz) orbitals anti-

bonding. Three d-d transitions originating in the nonbonding dxy orbital are possible. Two d-d transitions are observed at 13.80 kK and 23.00 kK[45] but the third is covered by the more intense charge transfer transitions. These charge transfer bands arise from the excitation of an electron from the highest filled π bonding molecular orbital (associated mainly with the oxygen atom) to the d orbitals located on the metal atom.

Subsequent studies[70-72] have confirmed these assignments for the d-d transitions but have disagreed with the charge transfer scheme for observed transitions. In these studies it was proposed that the scheme should be modified to include a substantial contribution from the halogen π orbitals in the bonding e_π level.

Binuclear molybdenum (V) complexes also show peaks at 14 and 22.26 kK. In this case the second peak is enhanced by dimerization. There appears to be no characteristic peak for a Mo - O - Mo system, although in one study a peak occurring at 39 kK was considered indicative of this grouping[73]. However little evidence was proposed on which to base this claim.

In studies[74,75] of molybdenum (VI) dioxo complexes, bands occurring in the region 27-30 kK were assigned to transitions of the type Mo ← O. A later study disagreed with these assignments and suggested that bands in this region are ligand to metal or ligand to ligand transitions. It was then suggested that terminal oxygen to molybdenum transitions occurred in the vicinity of 50 kK on the basis that bands had been found in this region in $[MoO_4]^{2-}$ and $[MoO_2S_2]^{2-}$ [77].

Metal ligand charge transfer transitions for molybdemum (VI) complexes have been assigned to peaks at 31.65 kK

(Mo ← O(L)), 27.25 kK (Mo ← N(L)) in $MoO_2$2oxine, and at 26.00 kK (Mo - S(L)) in molybdenum dithiocarbamate complexes[76]. It was found that Mo ← S charge transfer transitions occurred at lower energies than the corresponding Mo ← O transitions. Thus many molybdenum (VI) sulphur containing compounds are yellow or yellow-orange in colour as the Mo ← S band often tails into the visible region of the spectrum. The Mo ← S charge transfer band in molybdenum (V) xanthates appears 6 kK below that of the corresponding dithiocarbamate complexes, highlighting the stronger reducing powers of xanthates over dithiocarbamates. This agrees with experimental evidence that no molybdenum (VI) xanthate complex has been isolated, in every case the molybdenum (VI) is reduced to molybdenum (V) by the ligand.

2.1.7 Magnetic Properties of Molybdenum (V) and (VI) Complexes

The theoretical spin only moments for molybdenum (V) and (VI) complexes are 1.73 and 0.0 Bohr magnetons respectively[78]. The effects of spin-orbit coupling in the ground state $^2T_{2g}$ for molybdenum should give a value of the magnetic moment less than the theoretical value (i.e. $\mu \approx 1.0$ B.M.). However, the strongly asymmetric ligand field about the metal atom (resulting from oxo grouping) removes orbital degeneracy and hence $\mu \approx \mu_{s-o}$ (1.73 B.M.). Also a slight temperature independent paramagnetism is observed for some molybdenum (VI) complexes[79-81]. Magnetic moments close to the theoretical value are observed for mononuclear molybdenum (V) complexes but binuclear complexes have much lower moments as a consequence of the coupling of the spins of electrons in neighbouring molybdenum atoms (see appendix D). This is a consequence of exchange via the oxygen bridge in such complexes[51,52].

The magnetic properties of the compound $(NH_4)_2\ MoOCl_5$ have been studied in some detail[82,83] and the average magnetic moment over a wide range of temperatures is 1.67 B.M. The magnetic properties of linear bridged binuclear molybdenum (V) complexes have been discussed in the context of the complex Mo_2O_3(xanthate)[9]. Whether such a compound will be paramagnetic or diamagnetic appears to depend on the angle of twist of the two halves of the molecule about the oxygen bridge. When the dihedral angle is $\pi/4$ the most stable state is a triplet. As this angle decreases to zero the singlet state becomes more stable, leading to diamagnetism. The spin pairing mechanism leading to a lowering of the magnetic moment in such complexes has also been dealt with on a molecular orbital basis (see section 2.1.4 for details). In complexes with two oxygen bridges spin-spin interactions can occur through the formation of a metal-metal bond resulting from the close approach of the two metal centres necessitated by the geometry of the double oxygen bridge[51,52].

A table of reported magnetic moments for molybdenum (V) and (VI) complexes is shown in appendix D. From the table it can be seen that some molybdenum (VI) compounds have a significant magnetic moment[79-81]. For dimeric molybdenum (V) complexes those with a double oxygen bridge would be expected to have a lower magnetic moment than those with a single oxygen bridge, as the two metal atoms are closer together leading to a greater amount of spin pairing[51]. This prediction is generally borne out by the magnetic moments found for these compounds.

2.1.8 Stability Constants for Complexes of Molybdenum (V) and (VI)

Although comparatively few measurements have been made on the stabilities of molybdenum (V) and (VI) complexes, some interesting points arise from the data which are available (see appendix E). The methods which have been used to determine these constants are; spectrophotometry[84 et al.], partition between solvents[85 et al.] (usually chloroform and water), nuclear magnetic resonance measurements,[86 et al.] potentiometric titration[87 et al.], kinetic studies[88 et al.], catalytic effects[89], and paper electrophoresis[90]. In general, where studies have been made on molybdenum (V) and (VI) complexes with the same ligand, the molybdenum (VI) complex has been found the more stable by one or two orders of magnitude[91-94].

An interesting comparison between ligands involving oxygen and sulphur donors is afforded by the complexes of molybdenum with 8-quinolinol and 8-mercaptoquinolinol. The higher stability of the complexes with the sulphur containing ligand can be explained in terms of the higher covalency of the metal sulphur bond compared with the metal oxygen bond[95]. The increased stability of the 8-mercaptoquinolinol chelates can also be explained in terms of the presence of Mo ← S π bonds[95].

The stability constants of molybdenum (VI) complexes with 1,2,3,4-tetrahydro-8-mercaptoquinolinol are found to be 5-8 orders of magnitude less than those of 8-mercaptoquinolinol indicating that interaction with the ring π electron system is important in stabilizing these chelates[96]. This is further evidence of the importance of π bonding in these complexes.

2.1.9 Coordination Complexes of Molybdenum (V) and (VI)

Molybdenum forms a wide range of complexes with inorganic ligands such as fluoride, chloride, bromide, iodide, thiocyanate and cyanide ions. The chemistry of these types of complexes however has been extensively reviewed[2,12]. Oxo-species of molybdenum behave essentially as class (a) acceptors and as such form a wide variety of complexes with organic ligands containing oxygen or nitrogen donors. However molybdenum also forms some quite stable complexes with ligands containing sulphur atoms as donors.[97] Thus these complexes with sulphur containing ligands the molybdenum prefers SH or S^- donors to alcoholic -OH groups as shown by its strong preference for cysteine over serine as ligands. However molybdenum has little affinity for sulphur donors as found in ligands such as $(CH_3)_3PS$, $(CH_3)_3AsS$. In these complexes the sulphur atom is usually involved in extensive π bonding. Molybdenum (V) has also been shown to form well characterised complexes with ligands containing phosphorus[67,98] and arsenic[66] atoms. This illustrates the versatility of molybdenum in its coordination behaviour.

2.2 BIOLOGICAL ASPECTS OF MOLYBDENUM COORDINATION CHEMISTRY

2.2.1 Introduction

In recent years there has been a greatly increased interest in biological aspects of molybdenum chemistry as this element plays an important role in the metabolism of many living species[99-102], participating in a number of biochemical redox reactions, especially in the fixation of atmospheric nitrogen by plants[103,104]. Other redox systems in which molybdenum is known to play a part are the oxidation of xanthine and purines[105-109], and the reduction of nitrate[110-112]. The biological importance of nitrate reduction and nitrogen fixation cannot be overemphasised since they are the major routes of nitrogen incorporation for plants and hence for animals. In each of these systems the molybdenum is bound to an enzyme and in at least two, associated with a coenzyme, flavin adenine dinucleotide (FAD) (see Figure 2.6 showing structures of flavin prosthetic groups).

At this point it seems appropriate to include a brief explanation of the terms enzyme, coenzyme, prosthetic group, substrate and of their interrelationship. An enzyme is defined as being a protein with catalytic properties due to its power of specific activation[113]. The inclusion of the word protein is a generalisation from the fact that all enzymes which have been obtained in the pure state have proved to be proteins. The substance on which an enzyme acts, and which is activated by the enzyme, is termed the substrate of the enzyme[113]. In many cases an additional substance besides the enzyme and substrate is required in order that the reaction may proceed. Such coenzymes are a part of the catalytic mechanism and are found unchanged at the end of the

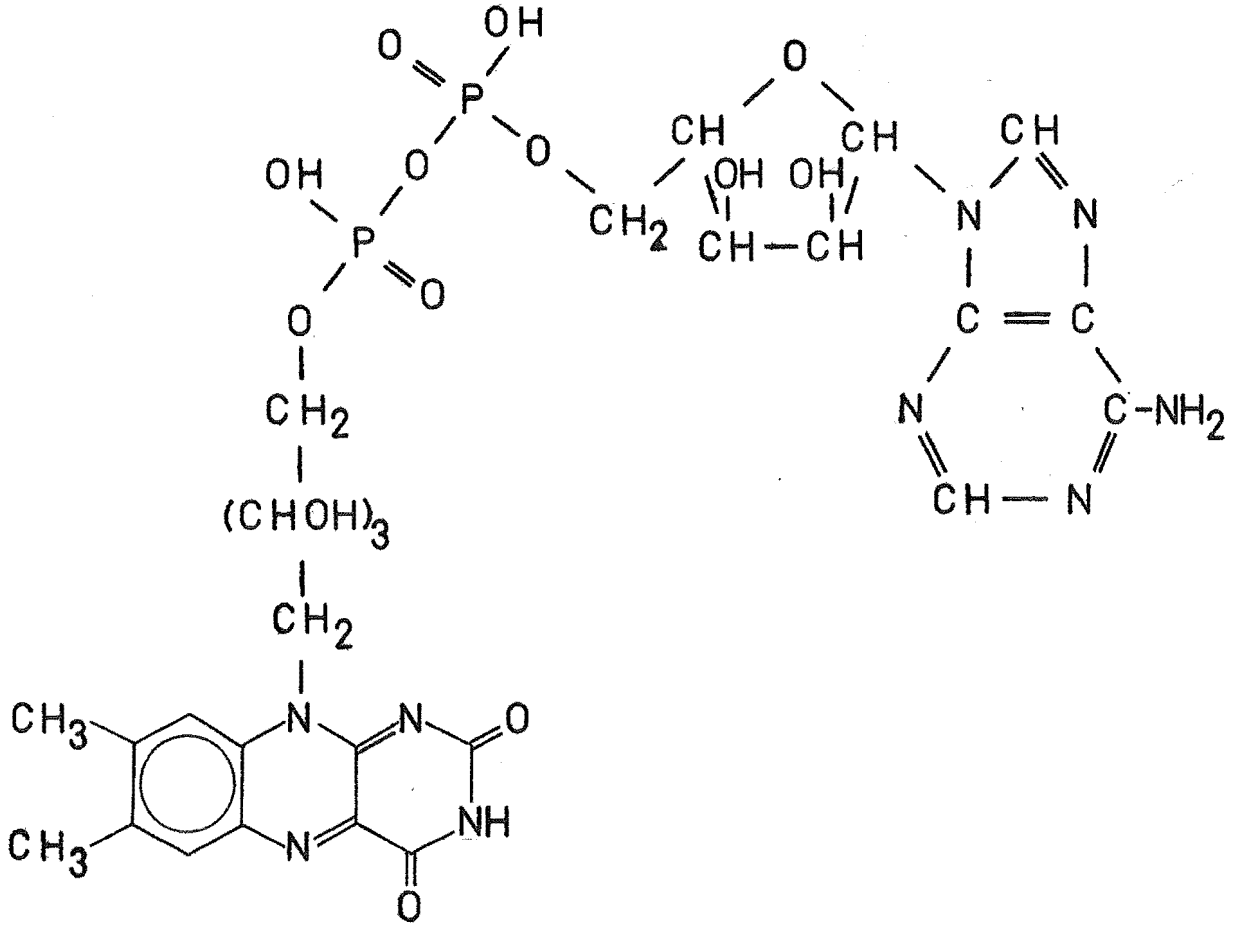


Fig. 2.6(a) Flavin-adenine-dinucleotide (FAD)

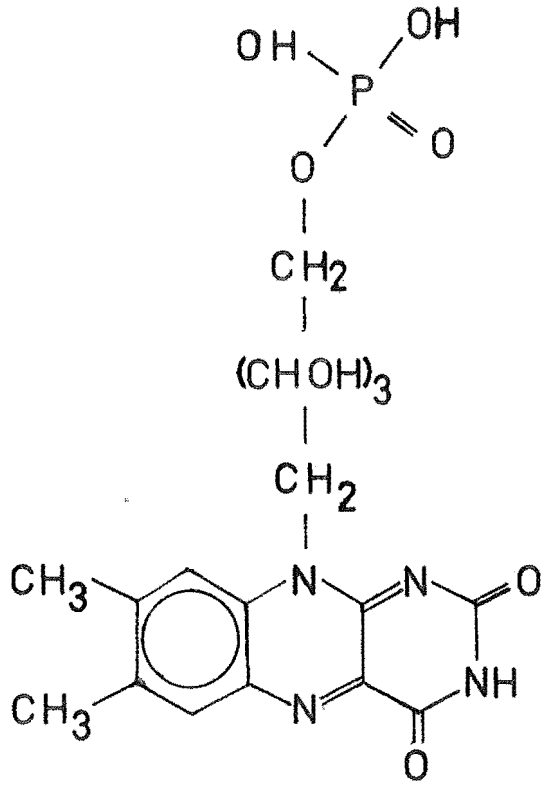


Fig. 2.6(b) Flavinmononucleotide (FMN)

reaction. In some enzymes prosthetic groups are attached to the protein and aid the enzyme action. The difference between a prosthetic group and a coenzyme is that a true prosthetic group undergoes its whole catalytic cycle attached to the same enzyme protein molecule while a coenzyme must migrate from one enzyme protein to another in order to fulfil its catalytic function[114].

All enzymes are made up of twenty different aminoacids. It is believed that the structure of the enzyme is specifically adapted to effect contact between amino-acids from different parts of the protein chain. Although the exact mechanisms by which enzymes convert one compound into another are unknown, a small area of the enzyme, called its active site, is thought to be of particular importance in determining the unusual properties of these biological catalysts. Presumably the substrate in the cell diffuses towards the enzyme and is strongly attracted to this active site. When it is attached there, the active amino acid residues cause a chemical change which converts the substrate into products. The products then diffuse away allowing another molecule of substrate to approach. The great majority of biological oxidations are really dehydrogenations, and involve the removal of two hydrogen atoms with a rearrangement of the bonds within the substrate. In many oxidation systems the substrates are not directly oxidised by molecular oxygen, but hydrogen transfer takes place through one or more intermediate substances (coenzymes such as flavins) which act as carriers[115]. The flavin nucleotides FMN and FAD (see figure 2.6) form one class of coenzymes which are involved in cellular oxidative reactions. Combined with certain enzymes to form flavoproteins,

they function as oxidants by accepting hydrogen atoms. As can be seen from figure 2.6,FMN contains phosphate, ribitol, and dimethylisoalloxazine units. It conforms to the general pattern of nucleotides although its carbohydrate group is a sugar alcohol and not a true sugar. Minus its phosphate group FMN becomes riboflavin (vitamin B_2). FAD contains adenine, ribose, two phosphate, ribitol,and dimethylisoalloxazine units. In both FMN and FAD it is the isoalloxazine skeleton which is active in hydrogen atom transfer.

This review will be limited to those aspects of molybdenum chemistry that are relevant to its biochemical functions and in particular its role in the process of nitrogen fixation.

2.2.2 Occurrence of Molybdenum Enzymes

Appendix F summarises the properties of most of the known molybdenum containing enzymes. Of particular interest is the fact that additional prosthetic groups, particularly flavins, are invariably present. In xanthine oxidase[116] and aldehyde oxidase[117], iron and FAD are also cofactors, whilst evidence regarding nitrate reductase indicates that molybdenum is the only metal present and the FAD generally found with the enzyme may not be an integral part of the system[118]. Nitrogenase appears to contain non-haeme iron also[119], but no coenzyme has yet been identified.

Xanthine oxidase is found in milk and the livers of various animal species. Aldehyde oxidase is present mainly in the liver, while nitrate reductase is widely distributed in plants and microorganisms. Nitrogenase was originally found in free living bacteria (Azobacter vinelandii and Clostridium pasteurianum) but it also appears likely to be present in bacteria involved in symbiotic nitrogen fixation in certain

plants.

Molybdenum is firmly bound to the enzymes and only in the case of nitrate reductase has the metal been reversibly dissociated[120]. The frequency with which a composition of two atoms of molybdenum per enzyme molecule occurs is of interest in view of the pronounced tendency of molybdenum compounds to be binuclear with the two molybdenum atoms close together and interacting through bridging oxygen atoms (see section 2.1). However there is no positive evidence for molybdenum molybdenum interactions in any of the enzymes.

2.2.3 Oxidation State of Molybdenum

From the information in section 2.1 it becomes evident that the oxidation states of molybdenum to be expected in aqueous environments are +6 and +5. However the +5 state is rather easily oxidised by oxygen in the physiological pH range unless complexed by certain types of ligands (see section 2.1). At present it seems to be generally accepted that these +5 and +6 states of molybdenum play the main roles in enzymatic action although there has been some recent evidence for the presence of the +4 state in xanthine oxidase[121,122]. Both the +5 and +6 states have been positively identified by complexing the molybdenum with 8-quinolinol[123,124] during the enzymatic reduction of nitrate. It was found that the change in oxidation state undergone by the molybdenum during the enzymatic process was +5 to +6. Paper chromatography was used to identify the oxidation state of the molybdenum atom by comparing the chromatograms with those of standard solutions. An alternative procedure was to extract the molybdenum into a chloroform solution of 8-quinolinol and paper chromatogram

the resulting solution. Both methods showed the presence of both molybdenum (V) and (VI).

Electron spin resonance (E.S.R.) signals characteristic of molybdenum (V) have been obtained from all the molybdenum enzymes[116,117,125,126]. Arguments concerning molybdenum reduction potentials are not conclusive since these depend to a great extent on the nature of the ligand[127]. However, it has been estimated[128] that the reduction potential of the molybdenum (V)/molybdenum (III) couple is between -0.6v and -1.0v at neutral pH values, which puts this couple outside the potential range of biological systems, particularly if the oxidant is a flavin (E_R^o = -0.25v). This prediction, combined with evidence on the stability of the molybdenum (III) ion in aqueous media[12], makes it unlikely that the +3 oxidation state of molybdenum plays any role in biochemical processes.

2.2.4 Binding Sites

Studies on complexes of simple ligands show that molybdenum in the +5 and +6 oxidation states exhibits its greatest affinity for ligands containing oxygen or SH and $S^=$ donors, although many complexes with ligands containing nitrogen atoms as donors are known (see section 2.1). It might be expected that in enzymatic systems molybdenum will be bound through the free carboxyl group of acidic aminoacids or the hydroxy groups of tyrosine or serine side chains. However, E.S.R. work on thio- complexes and inhibition studies with sulphuryl binding agents have shown that cysteine or cystine are more likely choices for binding sites[129-131]. Ultraviolet spectroscopy has been of little use in determining binding sites because both the molybdenum (V) charge transfer peaks

and the absorptions due to the prosthetic flavins occur in the same region (300-500 mμ)[132]. Iron-free xanthine oxidase has been reported[133,134], but its absorption spectrum appears to be identical with that for the native enzyme. Flavin-free nitrate reductase, which also contains no iron, has no absorption peaks at wavelengths greater than 280 mμ.

The use of E.S.R. relaxation studies of metal and metal-free systems has shown that molybdenum (V) in xanthine oxidase interacts with the flavosemiquinone radical contained in the coenzyme[135]. These effects were also noted in the glucose oxidase enzyme system[136]. It has also been shown that the behaviour of the molybdenum (V) species is altered when signals due to flavosemiquinone and iron are produced in the presence of substrate[117,137,138]. E.S.R. spectra obtained from xanthine oxidase show that the molybdenum atoms are in different chemical environments[139,140].

Furthermore, evidence has been found for changes in the ligand atom environment about molybdenum during the redox process[122,141]. There is a considerable body of evidence favouring some type of association of molybdenum in the active site in xanthine oxidase with one or more sulphur atoms. This evidence is mainly based on E.S.R. work in which it was suggested that the relatively high g_{av} values and low molybdenum hyperfine couplings in signals from the enzymes were analogous to those in molybdenum (V) thiol complexes[142] (see appendix G).

2.2.5 Function

As all of the molybdenum containing enzymes participate in redox reactions with substrates, it appears likely that the function of the metal ion is to participate in the binding of the substrate (where the versatility of molybdenum in adapting to different coordination environments becomes important (see section 2.1) and in the transfer of electrons between substrate and coenzyme or substrate and iron. The electron transfer sequence might be

$$\text{Substrate} \rightarrow Mo^{VI}/Mo^{V} \rightarrow \text{FAD/FADH}\cdot \rightarrow Fe^{3+}/Fe^{2+} \rightarrow O_2/O_2^{\cdot} \text{ or } O_2^{-}$$

where FADH· = flavosemiquinone (see figure 2.7).

At present little is known about the function of molybdenum in potentially the most interesting case, that of the enzyme nitrogenase[143], which is responsible for the fixation of atmospheric nitrogen. Although there have been speculations that molybdenum is the binding site for N_2 [144], evidence favouring this assumption is not conclusive[145]. Thus so far nothing positive has been established about the role of molybdenum in the enzyme.

2.2.6 Molybdenum Containing Flavin Systems

Since at least two of the molybdenum enzymes contain flavin as coenzyme and E.S.R. work has indicated an interaction between these components[134,135], complexes of molybdenum with flavins are of considerable interest. It has been reported[146] that flavins, in spite of their formal structural similarity to 8-quinolinol, have little affinity for metal ions in either their oxidised state, flavoquinones, or their completely reduced state, flavohydroquinones (see fig. 2.7).

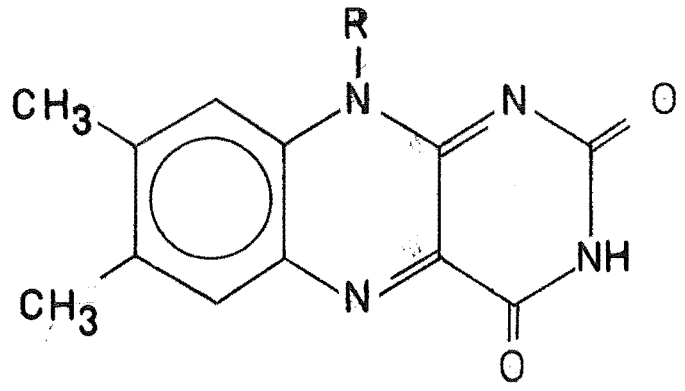


Fig. 2.7(a) Flavin in Quinoid State

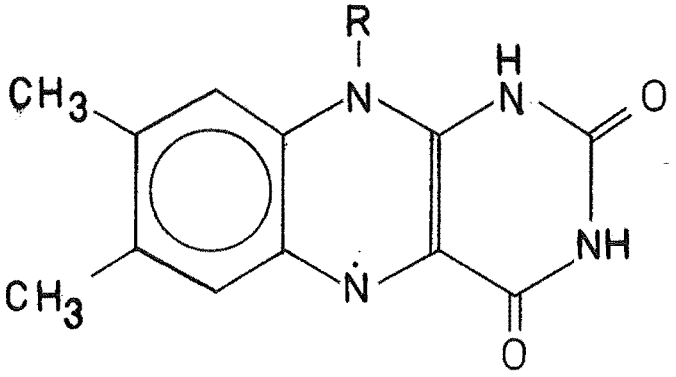


Fig. 2.7(b) Flavin in Semi-quinoid (Radical) State

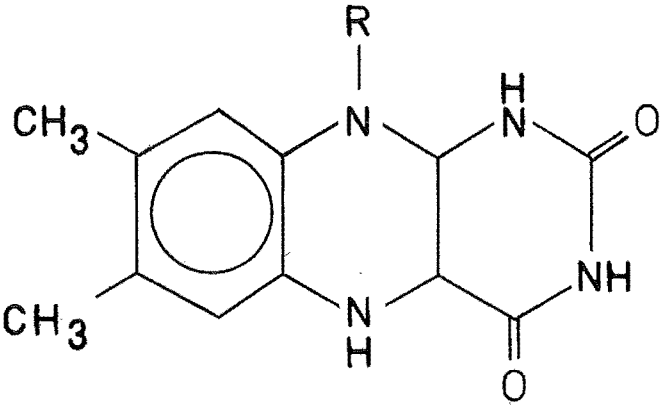


Fig. 2.7(c) Flavin in Hydroquinoid (Leuco) State

The intermediate flavosemiquinone state, however, forms relatively stable complexes with a number of metal ions in aqueous solution.

Recent work has been published on several flavin and metalloflavin complexes which have been characterised by X-ray structure determinations[147-160]. In one of these[158] involving a riboflavin-silver(1) complex it was found that the riboflavin offered two coordinating sites, one involving the normal N(5) - O(4) atoms (c.f. the coordination environment in 8-quinolinol complexes) and the other (the so-called secondary chelate site) involving the N(1) - O(2) atoms. The model showed that, far from sterically hindering this latter coordination site, the ribityl side-chain actively assisted in the coordination of the Ag(1) ion in spite of the weakness of alcoholic oxygen atoms as coordinating sites for this metal ion. In the case of molybdenum, with its known preference for this type of donor, the ribityl side chain could be even more important in the coordination.

It has been found[161,162] that molybdenum (VI) forms a strong complex with FMN at pH 2. In preliminary studies of the reaction between reduced flavins and molybdenum (VI), spectral evidence was found for increased concentration of the flavosemiquinone. This was suggested[163] as evidence that a complex had been formed between this entity and molybdenum, stabilizing the flavosemiquinone. Another study[164] of this reaction reported the presence of a red E.S.R.-inactive intermediate, while Hemmerich[165] found that when molybdenum (V) was added to a methylcyanide solution of flavin a spectrum characteristic of a semiquinone metal complex was obtained.

Thus it seems clear that an interaction does occur between molybdenum and flavins, the nature of which is still uncertain. In view of this it seems appropriate to review the evidence regarding the likely sites of coordination to molybdenum. All available evidence seems to implicate the ribityl side chain as at least one part of the coordination environment involving molybdenum. The ribityl group is a sugar alcohol and a considerable amount of evidence has been gathered about the interactions of sugars and other polyhydroxy compounds with molybdenum (V) and (VI)[166-168]. A wide range of polyhydroxy organic compounds have been examined and the first essential for complex formation with molybdenum appears to be the occurrence of hydroxy groups attached to adjacent carbon atoms. These hydroxy groups may be acidic or alcoholic, or combinations of both. There is some conflict over the number of hydroxy groups required by a polyhydroxy alcohol before it can form a molybdenum complex. It appears that three groups are necessary for a 1:1 complex and four for a 2:1 molybdenum:polyol complex. Studies on the molybdenum (VI) complex with gallic acid showed that the molybdenum was bound to the ligand through the hydroxy groups[169].

Using circular dichroism (C.D.) and optical rotatory dispersion (O.R.D.) techniques[167,170-173] on solutions of molybdenum (V) and (VI) with different sugars it was found that sugars which have three adjacent hydroxy groups, in a conformation in which they are able to complex at the apices of one face of the molybdenum octahedral coordinating sphere, gave the most stable complexes. It was noted[167] that as sugars are weakly acidic they are most likely to complex in weakly alkaline or neutral solutions. In the conformation in which

the three hydroxy groups are cis, they have an oxygen-oxygen distance of 2.7Å which compares very favourably with the oxygen-oxygen distance found in the structural determination of the E.D.T.A. complex of molybdenum (VI)[1]. These complexes were found to be stable over a wide range of pH values.

From these studies it can be seen that molybdenum is able to form stable complexes with groups such as ribityl side chains. There is also positive evidence that molybdenum does interact with the ribityl side chain. In a study[174] on the complexing behaviour of FMN a strong interaction was found with molybdenum (VI). Supporting evidence for involvement of the ribityl side chain came from the fact that there was no change in the ultraviolet spectrum of FMN on addition of molybdenum (VI). Such a change would be expected if the molybdenum ion disturbed the isoalloxazine resonance system by complexing to N(10) and the hydroxy group peri to it. A large change occurred in the optical rotation of FMN on addition of molybdenum (VI). This points to an interaction between the ribityl sidechain and molybdenum as the optical activity of FMN is due to the side chain.

2.2.7 Model Studies

The importance of elucidating the chemistry relating to the function of molybdenum in living processes has led a number of workers to study the interactions of molybdenum with ligands of biological interest. The amino acids form one group of ligands which are also important in living processes, especially in enzyme chemistry. Of the amino acids, histidine and cysteine are particularly important in view of their known participation in enzymatic action[175-178].

From spectrophotometric studies on the interaction of molybdenum (V) and (VI) with cysteine in solution it was concluded that molybdenum (VI) forms complexes in the pH range 4-6 in which cysteine functions as a bidentate ligand[179]. Only a weak complex was formed with molybdenum (V); oxidation occurred at high pH values. A similar study with histidine showed that a stable complex was formed with molybdenum (VI) while only a weak interaction could be detected with molybdenum (V). Coordination through amine and imidazole nitrogens was proposed. In later studies both histidine[180] and cysteine complexes[181] of molybdenum (V) were isolated and their structures determined[10,182]. These showed that in both cases the aminoacids were coordinating through their three functional groups, two nitrogens and an oxygen atom for histidine and oxygen, nitrogen and sulphur atoms for cysteine.

In a comprehensive study[183] of the interactions in solution between molybdenum (V) and (VI) and amino acids it was found that complexes were formed between asparagine, aspartic acid, alanine and threonine for molybdenum (VI) and between serine, aspartic acid and threonine for molybdenum (V). It was concluded that at least a tridentate ligand was necessary for stable complex formation with molybdenum (V). The nature and positions of the third complexing site was also found to be critical. With strong donors such as sulphur and imidazole nitrogen, complexes were stable in the pH range 2.5 - 9.5 whereas for weaker donors complexes could only be detected in the pH range 7-9.

The isolation of sulphur bridged complexes of histidine and cysteine has recently been reported[97,184] and the structure

of the histidine complex elucidated[185]. These results are significant as a sulphur bridged molybdenum system may be the active site in some of the molybdenum containing enzymes[186]. Sulphur donors labilize the replacement of bridging and terminal oxygen atoms and this may be important in the mechanistic path of enzymatic action[97]. Complexes with methionine, alanine and glycine have been isolated from acid (pH 1) solutions but these are not likely to have much physiological significance in view of the high acidity involved and also the low solubility and polymeric nature of these compounds[187].

Other types of ligands which have been studied include sugars[167], polyols[166] and α-hydroxyacids[168]. In these studies it was shown that molybdenum readily forms stable complexes in solution with ligands which provide at least three donor atoms.

2.2.8 Conclusion

The biochemical uniqueness of molybdenum appears to be due to its ability to coordinate to a wide variety of ligands, to exist in two or more oxidation states and to participate in both redox and ligand exchange reactions[188] via a number of different mechanisms. However, there is still uncertainty regarding the nature of molybdenum's role in enzyme action and as such much more study is needed on the chemistry of molybdenum in its +5 and +6 oxidation states.

C H A P T E R 3

STUDIES OF SIMPLE MODEL COMPOUNDS

3.1 INTRODUCTION

The role of molybdenum in biological systems is little understood. Because of the inherent complexity of biologically important metal complexes it seems important to develop an understanding of the chemistry of simpler model compounds of molybdenum in the +5 and +6 oxidation states and this in turn would provide an approach to the more complicated biological systems in which molybdenum is known to play a part (see chapter 2.2). The compounds studied in this chapter are all of molybdenum(VI). Some model compounds of molybdenum(V) with ligands of biological interest are discussed in chapter 4. With these model complexes it is hoped to develop methods of preparation and structural characterisation which can be applied to more complicated systems. The results obtained from the infrared studies are particularly relevant in this respect.

The types of compounds examined depended to some extent on preparative considerations, but in the course of this section of the work new preparative routes were developed and this extended the range of available compounds as well as the ease with which some could be obtained. The following classes of compounds were examined:

(i) Compounds of composition $MoO_2X_2L_2$ (X = Cl,Br; L = monodentate neutral ligands) and MoO_2X_2L' (L' = bidentate neutral ligands). These compounds contain neutral ligands and a cis dioxo MoO_2^{2+} grouping.

(ii) Compounds of composition $[MoO_3L]_n$, for which a polymeric structure given in figure 3.3(a) containing a μ,μ'-dioxo bridging system is proposed on the basis of analytical and infrared evidence.

(iii) Derivatives of the type MoO_2L_2, where L is a bidentate monoanionic ligand derived from a neutral molecule LH. These molecules were chosen to provide a range of donor atom pairs, namely: pentane-2,4-dione, equivalent O-O pair; ethane-1,2-diol (and other diols) a nonequivalent O-O pair; 2-amino-ethanol (O-N); and diethyldithiocarbamate, an equivalent S-S pair. The butane-2,3-diol complex of molybdenum(VI), although an example of class (iii), is discussed separately because of characterisation difficulties.

The results obtained from the infrared study will be presented first and preparative aspects will be discussed later in the chapter (sections 3.5 and 3.6).

3.2 INFRARED SPECTRA OF $MoO_2X_2L_2$ ADDUCTS

3.2.1 Introduction

Infrared vibrations which involve the metal atom and its interactions with surrounding attached atoms are important in that they yield information about both the strengths of the metal ligand bonds and the stereochemistry of the complex. The symmetry of the $MoO_2X_2L_2$ molecule varies according to the arrangement of the various attached groups about the metal atom. The two extremes are D_{2h} for an all *trans* molecule and C_1 for an all *cis* molecule with a symmetry of C_{2v} when one pair of ligands is in a *trans* arrangement. Since there are three pairs of ligands which can have the latter arrangement the total number of possible configurations is five, as shown

in Fig. 3.1. However it is possible to determine which , of these five possibilities, is the most likely to be encountered from a consideration of chemical evidence.

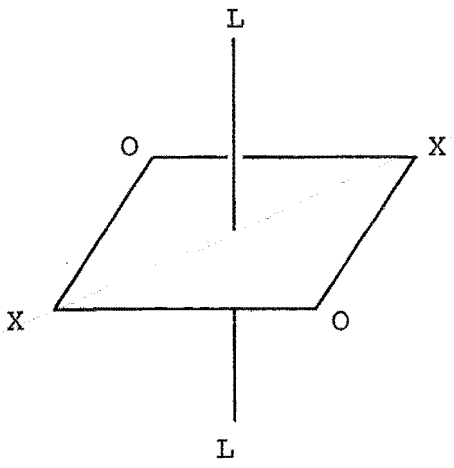
Firstly as two infrared active frequencies are found for the MoO_2^{2+} moiety and since this unit has been well characterised structurally by a number of X-ray structure analyses[4,26,41-44,189,190], it can definitely be said that in these compounds the MoO_2^{2+} group is cis (see chapter 2). This eliminates the D_{2h} all-trans molecule. Further it has been established as a general principle that in compounds of molybdenum the weakest donor groups will be found trans to the terminal oxygen atoms (see discussion of this in chapters 8 and 9). Also, X-ray structures have been reported for three $MoO_2X_2L_2$ molecules; MoO_2Br_2bipy[4], $MoO_2Cl_2(DMF)_2$[41], and $MoO_2Cl_2(DMSO)_2$[190] and in all these three cases the halogen atoms were found to be mutually trans while the other ligand atoms were mutually cis (i.e. trans to the terminal oxygen atoms). Thus in all these compounds the cis, trans, cis arrangement of the molecule $MoO_2X_2L_2$ is assumed having the point group symmetry C_{2v}.

For the unit $MoO_2X_2L_2$ (L here denoting only the coordinated atom of the ligand molecule) there will be 3N-6 = 15 normal modes of vibration. Forming the reducible representation;

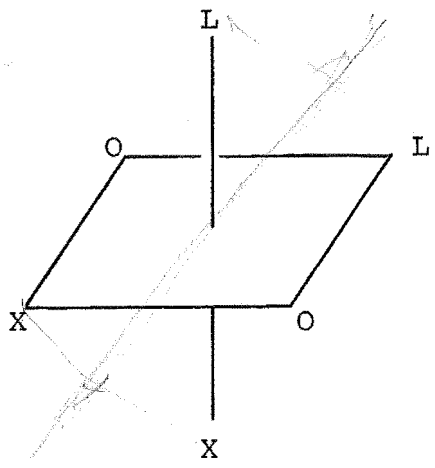
$$\Gamma_{red} = 7A_1 + 3A_2 + 5B_1 + 6B_2$$

however the following modes; $A_1+A_2+2B_1+2B_2$ correspond to rotational and translational modes of vibration and are accordingly removed, leaving

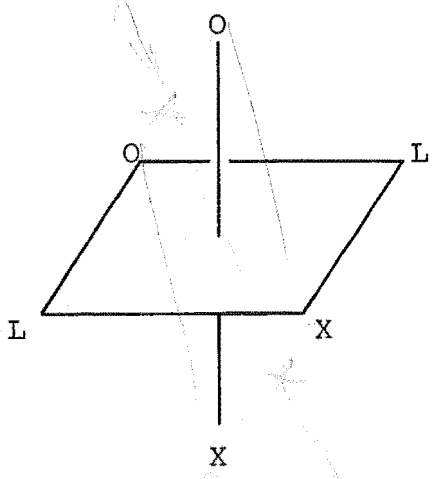
$$\Gamma_{vib} = 6A_1 + 2A_2 + 3B_1 + 4B_2.$$



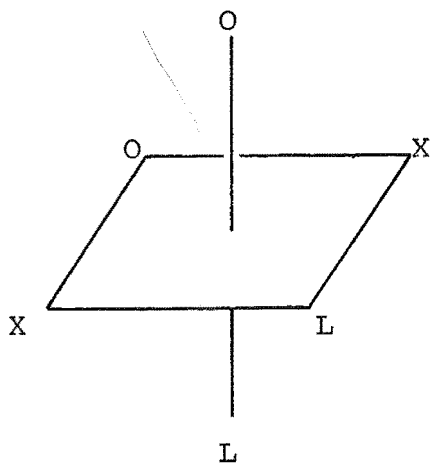
All trans D_{2h}



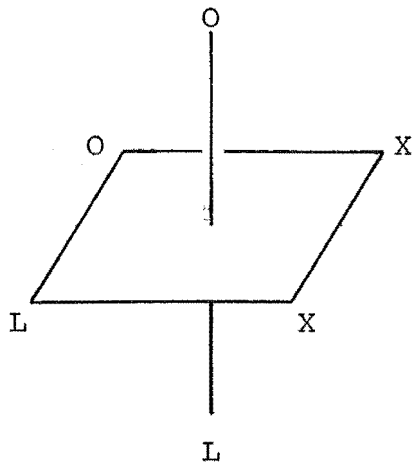
Trans-Cis-Cis C_{2v}



Cis-Cis-Trans C_{2v}



Cis-Trans-Cis C_{2v}



Cis-Cis-Cis C_1

Fig. 3.1 Possible Configurations of the $MoO_2X_2L_2$ Chromophone

Of these, the A_1, B_1 and B_2 modes are infrared active and the A_2, B_1 and B_2 modes Raman active. Thus one may expect 13 infrared active modes of vibrations associated with the $MoO_2X_2L_2$ unit.

3.2.2 Assignments of Infrared Stretching Frequencies

Of the vibrations associated with an $MoO_2X_2L_2$ moiety some are more readily identified than others. Vibrations associated with terminal oxygen atoms have been assigned by many authors (see the infrared section of chapter 2) and thus absorptions due to the molybdenum terminal oxygen stretching frequency are known to fall in the range 850-1000 cm^{-1}. In the cases discussed here two absorptions found in the 900-950 cm^{-1} region are assigned to $\nu(Mo=O)$ modes. Similarly the symmetric bending mode $\delta^s(MoO_2)$ has been assigned to an absorption occurring in the 360-390 cm^{-1} region[47] and this band appears insensitive to changes in the coordination environment of the central molybdenum ion.

Assignment of the metal-halogen stretching frequency can be readily achieved by comparison of the chloride and bromide spectra. The change in mass (and restoring force) alters the position of the metal-halogen stretching frequency. The metal-chloride stretching frequency appears as a strong sharp absorption, and the metal-bromide absorption, while well defined, is usually not as strong as that due to the chloride. The respective regions for these absorptions are 295-345 cm^{-1} and 180-225 cm^{-1}. It will now be shown that those modes above 100 cm^{-1} can be identified (see table 3.1).

In assigning absorptions due to the metal-ligand vibration for all $MoO_2X_2L_2$ complexes the same general principles

Table 3.1

Infrared Absorptions and Their Assignments For $MoO_2X_2L_2$ Compounds (1000-40 cm^{-1})

Cl/Me_3NO	Assignment	Cl/pyNO	Assignment	Br/pyNO	Assignment	Cl/DMSO	Assignment	Br/DMSO	Assignment
930	ν^s(Mo-O_t)	933	ν^s(Mo-O_t)	933	ν^s(Mo-O_t)	935	ν^s(Mo-O_t)	929	ν^s(Mo-O_t)
900	ν^a(Mo-O_t)	901	ν^a(Mo-O_t)	900	ν^a(Mo-O_t)	903	ν^a(Mo-O_t)	900	ν^a(Mo-O_t)
487	ν^s(Mo-L)	478	ν^s(Mo-L)	469	ν^s(Mo-L)	454	ν^s(Mo-L)	453	ν^s(Mo-L)
456	ν^a(Mo-L)	467	ν^a(Mo-L)	460	ν^a(Mo-L)	436	ν^a(Mo-L)	437	ν^a(Mo-L)
387	δ^s(MoO_2)	390	δ^s(MoO_2)	382	δ^s(MoO_2)	385	δ^s(MoO_2)	376	δ^s(MoO_2)
		340	ligand band	340	ligand band			356w	
320	ν^a(Mo-Cl)	320	ν^a(Mo-Cl)			340	ν^a(Mo-Cl)		
		305	ν^s(Mo-Cl)			295	ν^s(Mo-Cl)		
246	δ^a(MoO_2)	250	δ^a(MoO_2)	249	δ^a(MoO_2)	256	δ^a(MoO_2)	252	δ^a(MoO_2)
				224	ν(Mo-Br)			225	ν(Mo-Br)
		215	δ(MoL_2)	214	δ(MoL_2)	200	δ(MoL_2)	207	δ(MoL_2)
		182		185		180		170	
		122	δ($MoCl_2$)			128	δ($MoCl_2$)		
		110							
								92	δ($MoBr_2$)
								85	
		72	lattice vibrations			70	lattice vibration		lattice vibration
		55						62	

Table 3.1

Cl/Me_3AsO	Assignment	Cl/DMF	Assignment	Cl/Ph_3PO	Assignment	Br/PH_3PO	Assignment	Cl/THF	Assignment
937	$\nu^s(Mo\text{-}O_t)$	939	$\nu^s(Mo\text{-}O_t)$	947	$\nu^s(Mo\text{-}O_t)$	944	$\nu^s(Mo\text{-}O_t)$	958	$\nu^s(Mo\text{-}O_t)$
903	$\nu^a(Mo\text{-}O_t)$	905	$\nu^a(Mo\text{-}O_t)$	905	$\nu^a(Mo\text{-}O_t)$	903	$\nu^a(Mo\text{-}O_t)$	920	$\nu^a(Mo\text{-}O_t)$
430	$\nu^s(Mo\text{-}L)$	415	$\nu^s(Mo\text{-}L)$	415	$\nu^s(Mo\text{-}L)$	417	$\nu^s(Mo\text{-}L)$		
420	$\nu^a(Mo\text{-}L)$	390	$\nu^a(Mo\text{-}L)$	390	$\nu^a(Mo\text{-}L)$	391	$\nu^a(Mo\text{-}L)$		
348	$\delta^s(MoO_2)$	377	$\delta^s(MoO_2)$	378	$\delta^s(MoO_2)$	379	$\delta^s(MoO_2)$	388	$\delta^s(MoO_2)$
322	$\nu^a(Mo\text{-}Cl)$	335	$\nu^a(Mo\text{-}Cl)$	320	$\nu^a(Mo\text{-}Cl)$	335w		335	$\nu^a(Mo\text{-}Cl)$
						311vw	unassigned		
				295	$\nu^s(Mo\text{-}Cl)$	302w			
244	$\delta^a(MoO_2)$	252	$\delta^a(MoO_2)$	260	$\delta^a(MoO_2)$	259	$\delta^a(MoO_2)$	260	$\delta^a(MoO_2)$
		210	$\delta(MoL_2)$	218	$\delta(MoL_2)$	210	$\delta(MoL_2)$		
		198		202		202			
						180	$\nu(Mo\text{-}Br)$		
		165	$\delta(MoCl_2)$	157	$\delta(MoCl_2)$				
		145		152					
		98		138					
		72	lattice vibrations	72	lattice vibration	72	lattice vibration		
		48							

Table 3.1

Br/THF	Assignment	Cl/Bipy	Assignment	Br/Bipy	Assignment	Cl/ophen	Assignment	Br/ophen	Assignment	Cl/MeCN	Assignment
958	$\nu^s(Mo\text{-}O_t)$	938	$\nu^s(Mo\text{-}O_t)$	934	$\nu^s(Mo\text{-}O_t)$	938	$\nu^s(Mo\text{-}O_t)$	936	$\nu^s(Mo\text{-}O_t)$	960	$\nu^s(Mo\text{-}O_t)$
917	$\nu^a(Mo\text{-}O_t)$	904	$\nu^a(Mo\text{-}O_t)$	905	$\nu^a(Mo\text{-}O_t)$	904	$\nu^a(Mo\text{-}O_t)$	903	$\nu^a(Mo\text{-}O_t)$	920	$\nu^a(Mo\text{-}O_t)$
		475		468							
		450	ligand	444	ligand						
		425		418							
										411	ligand
380	$\delta^s(MoO_2)$	382	$\delta^s(MoO_2)$	375	$\delta^s(MoO_2)$	382	$\delta^s(MoO_2)$	366	$\delta^s(MoO_2)$	387	$\delta^s(MoO_2)$
		342	$\nu^a(Mo\text{-}Cl)$			335	$\nu^a(Mo\text{-}Cl)$			346	$\nu^a(Mo\text{-}Cl)$
						310	$\nu^s(Mo\text{-}Cl)$				
261	$\delta^a(MoO_2)$	241	$\delta^a(MoO_2)$	252	$\delta^a(MoO_2)$	238	$\delta^a(MoO_2)$	258	$\delta^a(MoO_2)$	250	$\delta^a(MoO_2)$
				218	$\nu(Mo\text{-}Br)$	210vw		216	$\nu(Mo\text{-}Br)$		
		208		192		192		192			
		192	$\nu(Mo\text{-}N)$	178	$\nu(Mo\text{-}N)$	180	$\nu(Mo\text{-}N)$	178	$\nu(Mo\text{-}N)$		
		145				165					
		125	$\delta(MoCl_2)$			150	$\delta(MoCl_2)$				
		112				122					
				100							
				88	$\delta(MoBr_2)$						
						72					
						60	lattice vibration				
				52	lattice vibration						

were used. After identifying the bending and stretching modes of the MoO_2^{2+} group, the metal-halogen stretching mode and also identifying absorptions which originate from the ligand, there were generally few remaining unassigned absorptions in the spectrum above 200 cm^{-1}. Since the two ligand donor atoms are mutually cis there should be two reasonably closely spaced medium to strong absorptions associated with the metal-ligand symmetric and asymmetric stretches. These were usually readily identifiable (see table 3.1) and it was of interest at this point to compare the values obtained above with those found for the respective ligands for other metals, while allowing for differences in mass and oxidation state.

The first case to consider is that of the trimethylamine-N-oxide complex $MoO_2Cl_2((CH_3)_3NO)_2$. A detailed analysis of the spectrum of this compound illustrates the arguments used in the assignment of the various vibrations in this class of compounds. On the general principles established above, bands appearing at 900 and 930 cm^{-1} are assigned to ν(Mo=O). These present assignments, however, are at variance with those previously reported by Choplin, Kauffmann and Rohmer[191] of ν(Mo=O) to absorptions at 938 and 960 cm^{-1}. The present assignments are to be preferred as these are stronger and better resolved bands and thus more likely to be associated with this vibration. It has been found that strong π bonding ligands compete with the terminal oxygen atoms for the available empty πd orbitals of the molybdenum atom. In the case of the $MoO_2X_2L_2$ compounds the ligands (L) are trans to the terminal oxygen atoms and are thus directly competing with them for the available empty πd orbitals, whereas the halogen

atoms are cis to the terminal oxygen atoms and are not directly competing with them. Thus changing the halogen atom causes little or no change in the positions of the ν(Mo=O) absorptions while changing L has a much greater effect (see table 3.1). This competition for the πd orbitals lowers the multiplicity of the molybdenum oxygen bond, with a consequent lowering of the ν(Mo=O) frequencies. Thus only in the case of the weak π donor ligand CH_3CN does the value of the ν^s(Mo=O) remain near 960 cm^{-1}.

The metal-ligand stretching vibrations, for the complex $MoO_2Cl_2((CH_3)_3NO)_2$, have been assigned to strong absorptions appearing at 456 and 487 cm^{-1}. Previous assignments of metal-ligand stretching vibrations for this ligand have been in the range 380-470 cm^{-1} [192]. The present assignment at the top of the range quoted whichis to be expected in view of the high oxidation state of molybdenum and the strong bonds it forms with oxygen donors. On the general principles established in the $(CH_3)_2NO$ complex two absorptions are assigned for the complex $MoO_2Cl_2((CH_3)_3AsO)_2$ at 420 and 430 cm^{-1} for the molybdenum-ligand stretching frequencies. There is fair agreement with the tentative assignment presented by Choplin Kauffmann and Rohmer[191] but without supporting evidence.

The molybdenum-ligand stretching modes for the bromine and chlorine complexes of pyridine-N-oxide (pyNO), $MoO_2X_2(pyNO)_2$, are assigned to two bands in the 460-480 cm^{-1} region. It was of interest to find that there has been a previous assignment of ν(Mo-L) for a molybdenum(II) chlorine complex to absorptions occurring from 390-460 cm^{-1} [193]. The increase in formal oxidation state would account for the increase in frequency found in this case. Other assignments of ν(M-L) for

different metals have been made of absorptions in the range 300-450 cm^{-1} [194-199].

For the dimethylsulphoxide (DMSO) complexes $MoO_2X_2(DMSO)_2$, (X = Cl, Br) a pair of sharp bands found in the region 435-455 cm^{-1} was assigned as the two expected vibrational modes. Bands close to this region (416 and 420 cm^{-1}) have been assigned by Kauffmann and Leroy[373] as metal-ligand stretches for DMSO complexes of the uranyl ion UO_2^{2+}. In this study absorptions occurring at 390 and 415 cm^{-1} are assigned to the metal ligand interaction for the chlorine and bromine complexes of dimethylformamide (DMF), $MoO_2X_2(DMF)_2$. For the complexes of triphenylphosphine oxide $MoO_2X_2(PhPO)_2$ (X = Cl,Br), although there is often difficulty associated with the assignments of these metal-ligand stretching vibrations[192] it was found that assignments of the modes could be made with reasonable confidence.

For complexes of the ligands α,α'-bipyridyl (bipy) and o-phenanthroline (ophen) containing bidentate nitrogen donors, the molybdenum ligand stretching modes are assigned to absorptions which are found in the vicinity of 200 cm^{-1}. There has been some general difficulty in assigning metal-ligand stretching frequencies in bipy and ophen complexes because these absorptions are usually only of medium strength and occur at rather low frequencies[200-205].

Tetrahydrofuran (THF) has been found to be a weak ligand and few complexes of this ligand have been prepared[206,207]. Unstable molybdenum(VI) complexes of composition $MoO_2X_2(THF)_2$, (X = Cl,Br) could be isolated but an analysis of their infra-red spectra showed that there were no spectral bands down to 200 cm^{-1} which could be assigned to molybdenum-ligand

stretching modes. This probably reflects the general weakness of the metal ligand bond in complexes of THF. In the case of the acetonitrile complex $MoO_2Cl_2(CH_3CN)_2$, as with the THF complexes, no bands appeared above 200 cm^{-1} which could be assigned to a molybdenum-nitrogen stretching mode. This is as expected in metal nitrile complexes[202,203,208-210].

3.2.3 Bending Modes: Computer Assisted Assignments

As has been stated in the introduction there are thirteen infrared active vibrational modes for the $MoO_2X_2L_2$ entity (considering only the attached donor atom of the ligand L). The stretching modes involving the attached atoms have been readily identified as has the bending mode involving the terminal oxygen atoms. However, the assignment of the bending modes involving the other attached atoms presents a problem. It is difficult even on a qualitative basis to distinguish between the bending modes of the various types (O=Mo-X), (O=Mo-L), (X-Mo-X), (L-Mo-L) and (X-Mo-L).

However, it was found that use of a program[288] enabled an approximate set of values for these various bending modes to be obtained. Input data for the program were values of positional parameters (values of the coordinates were based on all atoms being placed on three orthogonal axes) and masses for the atoms and approximate values of the force constants for all vibrational modes. Output data obtained from the program were a set of thirteen frequencies, values of the root mean square amplitudes of vibration for each of the seven atoms involved in each vibrational mode, and the symmetry species of each vibrational mode.

As some of the absorptions in the sample compound had been assigned to particular modes of vibration, the force constants for these particular modes could be adjusted until the predicted and observed frequencies matched each other. Also since the stretching and bending modes of the MoO_2^{2+} group had been well characterised the relationship between $\nu(Mo{=}O)$ and $\delta(MoO_2)$, and in particular the relationship between the force constants of these modes, is known independently and, assuming this ratio remains relevant for the MoX_2 and MoL_2 groups, the information obtained provided the means of narrowing the region of the spectrum in which these latter bending modes would be expected to be found.

The calculations were based on the molecule $MoO_2Cl_2(DMF)_2$. This molecule had the twin advantages that an X-ray structure analysis had been reported[41] and a clear, well resolved spectrum was available. It was not considered desirable to make the initial calculations on the simpler complex ion $[MoO_2Cl_4]^{2-}$ as the configuration had been incorrectly assumed to be <u>trans</u> dioxo[39] and this may have invalidated the assignments made in this paper. The results obtained from the last calculation are shown in table 3.2. The significant points which emerge from this calculation are that there is an asymmetric bending mode involving the MoO_2^{2+} group predicted in the vicinity of 250 cm^{-1}. Bending modes involving the ligand atoms (L) are predicted <u>ca</u>. 200 cm^{-1} and the halogen atoms (X) <u>ca</u>. 150 cm^{-1}.

On the basis of these results absorptions found in the observed spectra of the $MoO_2X_2L_2$ complexes could be assigned. These assignments are presented in table 3.1.

Table 3.2

Comparison of Observed and Calculated Spectrum for $MoO_2Cl_2(DMF)_2$

Observed Frequency (cm^{-1})	942	907	415	390	380
Calculated Frequency (cm^{-1})	945	906	413	388	380
Symmetry Species	A_1	B_2	A_1	B_2	A_1
Main Component of Vibration (Calculated Spectrum)	$\nu^s(Mo\text{-}O_t)$	$\nu^a(Mo\text{-}O_t)$	$\nu^s(Mo\text{-}L)$	$\nu^a(Mo\text{-}L)$	$\delta^s(MoO_2)$
Observed Frequency (cm^{-1})	335br	-	infrared inactive	-	252
Calculated Frequency (cm^{-1})	351	299	291	278	276
Symmetry Species	B_1	B_1	A_2	A_1	B_2
Main Component of Vibration (Calculated Spectrum)	$\nu^a(Mo\text{-}Cl)$	MoCl stretch, bend		$\nu^s(Mo\text{-}Cl)$	$\delta^a(MoO_2)$
Observed Frequency (cm^{-1})	210	198	infrared inactive	165	145
Calculated Frequency (cm^{-1})	222	191	175	140	136
Symmetry Species	A_1	B_1	A_2	B_2	A_1
Main Component of Vibration (Calculated Spectrum)	$\delta^s(ML_2)$	$\delta(ML_2)$ out of plane		$\delta^s(MoCl_2)$	$\delta^s(MoCl_2)$

3.2.4 Modifications in the Ligand Spectra For $MoO_2X_2L_2$ Complexes

This section is concerned with those absorptions which involve modes of vibration of the ligand. A comparison of the infrared spectrum of the ligand (before coordination) and that of the complex gives indirect information on the strength of the metal ligand bond. The most relevant changes are concerned with modifications of the stretching modes derived from bonds which are alpha to the metal ligand bond, e.g. ν(X-O) in R_nXO complexes (n = 2 or 3, X = As, C, N, P). The modification of the ligand spectrum upon coordination also confirms that the method of attachment of the ligand to the metal atom was in all cases through an oxygen atom in these complexes.

Ligands of the general type R_nXO (n = 2 or 3, X = As, C, N, P) have canonical forms of the type:

$$\underset{\text{I}}{R_n\overset{+}{X}\text{-}\overset{-}{O}} \longleftrightarrow \underset{\text{II}}{R_nX=O} \longleftrightarrow \underset{\text{III}}{R_n\overset{-}{X}\equiv\overset{+}{O}}.$$

In the free ligands the bond order of the X-O bond was *ca.* two, resulting from the resonance between the forms I, II and III. Coordination via the oxygen atom will favour form I and result in a lowering of the ν(X-O) frequency. These general trends were noted in the complexes of DMSO

$$[\nu_{free}(S-O) = 1102\ cm^{-1},\ ^{211}\ \nu_{complex}(S-O) = 950\ cm^{-1}],$$

$$Ph_3PO[\nu_{free}(P-O) = 1193\ cm^{-1}\ ^{212},$$

$$\nu_{complex}(P-O) = 1150\ cm^{-1}],$$

Table 3.3

Infrared Assignments of $MoO_2X_2L_2$ Complexes from 4000-500 cm^{-1}

Me_3NO[243]	Cl/Me_3NO	Assignment	Ph_3PO[212]	Cl/Ph_3PO	Br/Ph_3PO	Assignment
3068	3020	ν(C-H)	3065	3040	3040	ν(C-H)
3003	2997	ν(C-H)	1594	1592	1590	ν(C-C)
1482	1485	CH_3 def.	1578	-	-	ν(C-C)
1472	-					
1457	1452		1487	1489	1489	ν(C-C)
1398	1392	δ(CH_3)	1444	1423	1435	ν(C-C)
1240	1242	CH_3 rock	1335	1315	1315	ν(C-C)
1124	1130		1314	-	-	Combination
	960	ν^a(C-N)	1281	-	-	β(C-H)
946						
	952		1188	1170sh	1180sh	β(C-H)
	946	ν^s(Mo-O_t)	1168	1155sh	1160sh	β(C-H)
936	938	ν^s(N-O)	1193	1141	1152	ν(P-O)
	918	ν^a(Mo-O_t)	1122	1119	1121	X-sensitive
	900	ν^a(N-O)	1097	1086	1091	overtone
	740br	ν^s(C-N)	1074	1071	1074	β(C-H)
			1028	1028	1030	β(C-H)
			997	997	998	p ring
			973	-	961sh	γ(C-H)
				942	947	ν^s(Mo-O_t)
				901	907	ν^a(Mo-O_t)
			860	848	850	γ(C-H)
			843			
			755	755	758	γ(C-H)
			750sh	749	752	
			621	721	724	X-sensitive
				715sh		
			698	690	690	ϕ(C-C)
			619	619	619	α(C-C)
			542	537	539	X-sensitive
				522	521	

Table 3.3

DMSO[211]	Cl/DMSO	Br/DMSO	Assignment	Bipy[242]	Cl/Bipy	Br/Bipy	Assignment
2979	3012	3002	ν^a(C-H)	3086	3107	3130	ν(C-H)
				3078		3100	
2908	2893	2894	ν^s(C-H)	3061		3080	
				3054			
1419	1422			1579	1601	1603	ν(C-N)+ν(C-C)
		1418	δ^a(CH_3)		1598	1591	
1405	1415			1553	1500	1503	
	1321	1322	δ^s(CH_3)	1448	1480	1484	ring strain
1304							
	1311	1300		1410	1450	1458	ring strain
1016	1030	1036			1319	1320	H bend + ring strain
				1248	1269	1270	ring strain
1009	1025	1030	Methyl rock		1247	1245	
							resonance dep.,
999	992	995		1210	1223	1228	ring strain
					1171	1174	
	951	969	ν^a(S-O)		1152	1156	H in plane
1102				1138	1100	1110	bend
	941sh	954	ν^s(S-O)			1100	
				1093	1071	1073	ring strain
	921	921	ν^s(Mo-O_t)	1083	1060	1061	+ bend
				1063	1042	1044	
	890	890	ν^a(Mo-O_t)		1026	1029	H out of plane bend
				991	1016	1017	ring breathing mode
	722	727			934	935	ν^s(Mo-O_t)
689			ν^a(C-S)		904	904	ν^a(Mo-O_t)
	719	722					
					772	776	H out of plane bend
672	680	686	ν^s(C-S)	738			
					731	732	
					657	657	
				651	649	649	ring bend
					636	638	

Table 3.3

PyNO[194]	Cl/PyNO	Br/PyNO	Assignment	DMF[213]	Cl/DMF	Assignment	CH_3CN[215]	Cl/CH_3CN	Assignment
	3114	3112	ν^a(C-H)	2940		$\nu^a(CH_3)$	3164	3250	combination
	3045	3045	ν^s(C-H)	2928		ν(C-H)	3003	3001	ν^a(C-H)
1610	1610	1610	ring def.	2860		$\nu^s(CH_3)$	2944	-	ν^s(C-H)
						ν(C-O)			
1475	1470	1467	ring def.	1679	1635	ν(C-N)	2628	-	combination
						δ(C-H)			
	1410	1408					2411		combination
				1490	1490sh	δ(C-H)			
	1319	1331	CH in plane def.				2293		combination
				1460		$\delta^a(CH_3)$			
	1230	1247				out-of-plane	2254	2325	ν(C-N)
				1442	1433	$\delta^a(CH_3)$			
						in-plane			
1243	1212	1214	ν(N-O)				2204	2300	combination
						ν(C-O)			
				1389	1378	ν(C-N)			
	1205sh					δ(C-H)			
	1170	1176		1250	1248	δ^a(C-N-C)	1443	1420	$\delta^a(CH_3)$
1183									
	1165	1155		1095	1119	CH_3 rock in-plane	1376	1377	$\delta^s(CH_3)$
	1145		CH in plane def.	1067	1058	CH_3 rock in-plane	1047	1028	CH_3 rock
					1010				
	1141				974			960	ν^s(Mo-O_t)
	1082	1096			942	ν^s(Mo-O_t)	917	939	ν(C-C)
1078									
	1069	1072			907	ν^a(Mo-O_t)		920	ν^a(Mo-O_t)
	1041	1051		866	860	δ^s(C-N-C)	749	795	overtone

(contd)

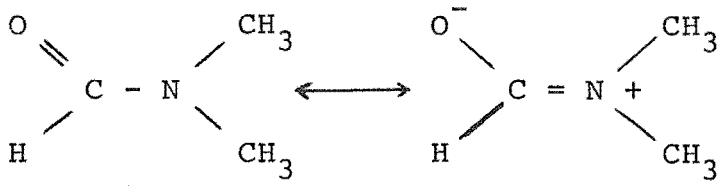
Table 3.3

PyNO[194]	Cl/pyNO	Br/pyNO	Assignment	DMF[213]	Cl/DMf	Assignment	CH_3CH[215]	Cl/CH_3CN	Assignment
1025	1014	1024	ring breathing	660	683	(OCN)		679	combination
887	979	996 968	CH out of plane						
	927	929	$\nu^s(Mo\text{-}O_t)$						
	889	898	$\nu^a(Mo\text{-}O_t)$						
840	830 810	835 818	$\delta(N\text{-}O)$						
777	772 754	770 767	CH out of plane						
680	666 660 631	669 740	ring skeleton def.						

PyNO[ν_{free}(N - O) = 1243 cm^{-1}, $\nu_{complex}$(N - O) = 1210 cm^{-1}].

The case for DMF is discussed in more detail because of modifications in skeletal modes upon coordination.

From a consideration of the two canonical forms of the ligand DMF it can be seen that coordination to a metal centre



I II

via the oxygen atom should enhance the importance of form II, and lead to a lowering of ν(C-O) and a corresponding increase in ν(N-C). However, a normal coordinate analysis[213] indicates that ν(C-O), ν(C-N) and δ(C-H) are strongly coupled and thus changes in the peaks in the regions expected for ν(C-O) and ν(C-N) are not meaningful. Nevertheless, the O-C-N bending mode in the free ligand is not coupled and is a better choice for frequency shift comparisons. The shift in the δ(N-C-O) mode has been shown to increase with increasing strength of the metal oxygen bond[214]. This vibrational mode has been found to absorb at 683 cm^{-1} in the complex $MoO_2Cl_2(DMF)_2$, a value which puts the strength of the molybdenum oxygen bond as comparable with that found for complexes of DMF with cobalt, nickel and copper[214].

In the case of complexes of nitrides it has been reported[215] that coordination of the C ≡ N group to a metal centre via the nitrogen atom causes a positive shift in the value of ν(C-N). In the free CH_3CN molecule ν(C-N) is found at 2257 cm^{-1} while

in the complex $MoO_2Cl_2(CH_3CN)_2$, ν(C-N) is found at 2324 cm^{-1} showing that coordination has occurred via the nitrogen atom.

3.3 $[MoO_3L]_n$ COMPLEXES

Complexes of unknown structure analysing to the formula MoO_3L (L = monodentate aprotic ligand) were synthesised by refluxing MoO_3 with excess ligand. That the reaction did not involve condensation was shown by the fact that no molybdenum blue was formed during the dissolution (c.f. MoO_2L_2 compounds). The MoO_3 dissolved in the liquid ligand and the complex was isolated by precipitation with a suitable solvent. Since these complexes were derived from MoO_3 and their infrared spectra showed marked similarities to that of MoO_3 consideration of the structure of this oxide is relevant.

In crystalline MoO_3[216] the molybdenum atom was shown to have sixfold coordination with the oxygen atoms arranged about the molybdenum in a distorted octahedron. The structure can be considered to consist of sheets formed from octahedra sharing edges with two adjacent octahedra, and corners with two other octahedra (see figure 3.2(a)). The arrangement of oxygen atoms about a single molybdenum atom is shown in figure 3.2(b). The most interesting points about this structure are the presence of a single terminal oxygen atom and the extensive bridging system of oxygen atoms.

In proposing a structure for the $[MoO_3L]_n$ complexes a number of points must be noted. First, there is the similarity in composition, with the complexes derived from MoO_3 retaining this unit. The reaction which produced these complexes is different from that used to produce the MoO_2L_2 complexes. In the latter case, heating the trioxide with the ligand results in the formation of molybdenum blue which must be removed from

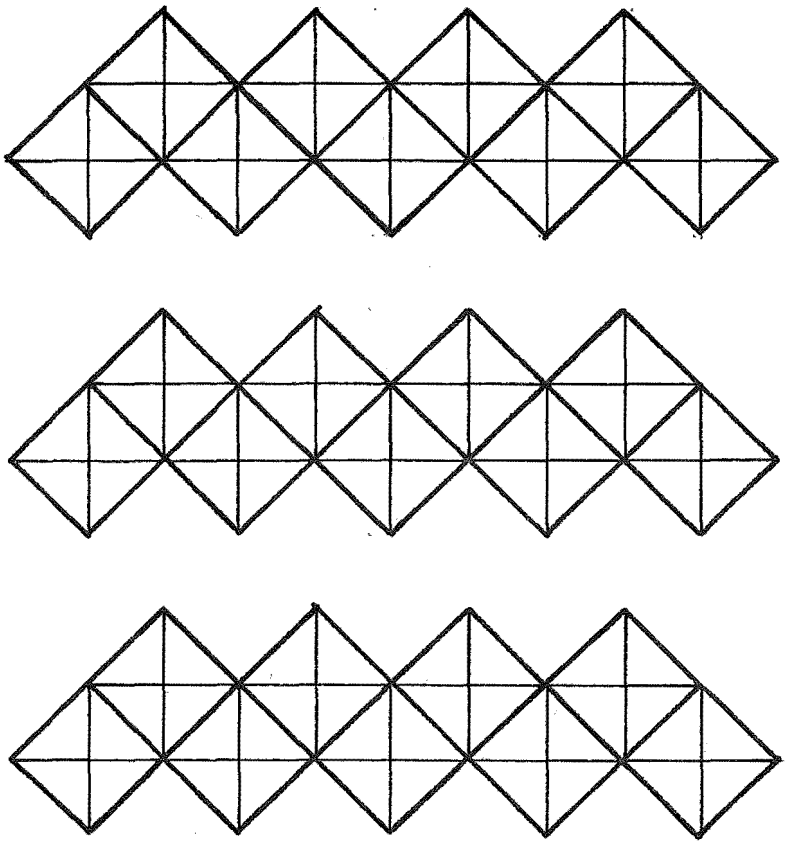


Fig. 3.2(a) Arrangement of layers in MoO_3

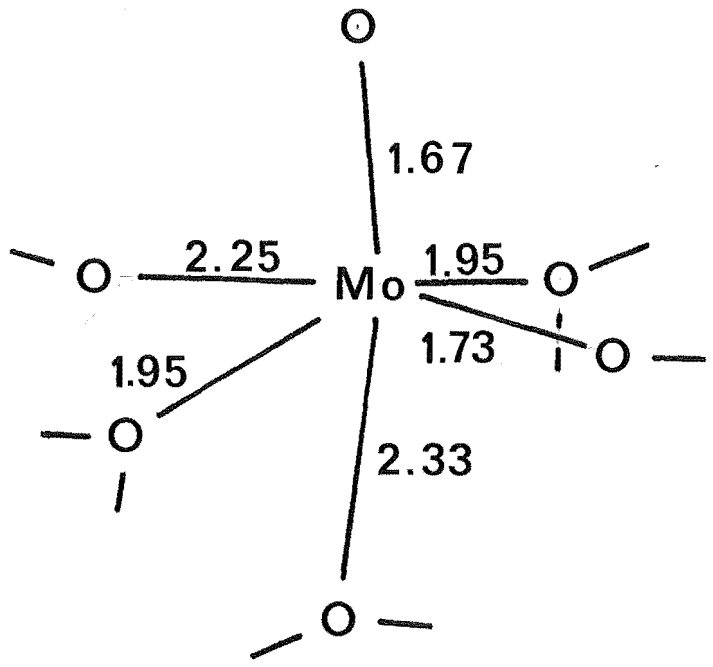


Fig. 3.2(b) Arrangement about Molybdenum in MoO_3

the reaction mixture. In the former case, all that appears to happen during the reaction is the gradual dissolution of the oxide in the ligand upon heating.

A comparison of the infrared spectra of these compounds with the spectrum of the trioxide showed close similarities in band shape and position, both showing a single infrared absorption corresponding to one terminal oxygen atom and also absorptions due to a μ,μ'-dioxo bridging system (with only slight modifications of the latter bands in the complex). On the basis of this evidence it is inferred the structure is as shown in fig. 3.3(a) involving the breaking of the longest and presumably weakest oxygen molybdenum linkage in the trioxide on formation.

The complex with bipyridyl cannot conform to precisely the same structure, nor was it obtained by the same method. It was synthesised using the butane-2,3-diol complex as an intermediate. The infrared of this complex shows two bands in the region expected for a cis-dioxo group (880-950 cm^{-1}) and also absorptions due to the vibrations of a μ,μ'-dioxo bridge. It is therefore suggested that this complex represents a dinuclear structure as shown in fig. 3.3(b).

A full analysis of the infrared spectra of these compounds is presented in table 3.4. The value for δ(OCN) in the DMF complex at 741 cm^{-1} (c.f. $MoO_2Cl_2(DMF)_2$ at 683 cm^{-1}) and the lowering of ν(S-O) in the DMSO complex to 947 cm^{-1} indicate that the ligand is bonded to molybdenum in the expected manner via the oxygen atoms.

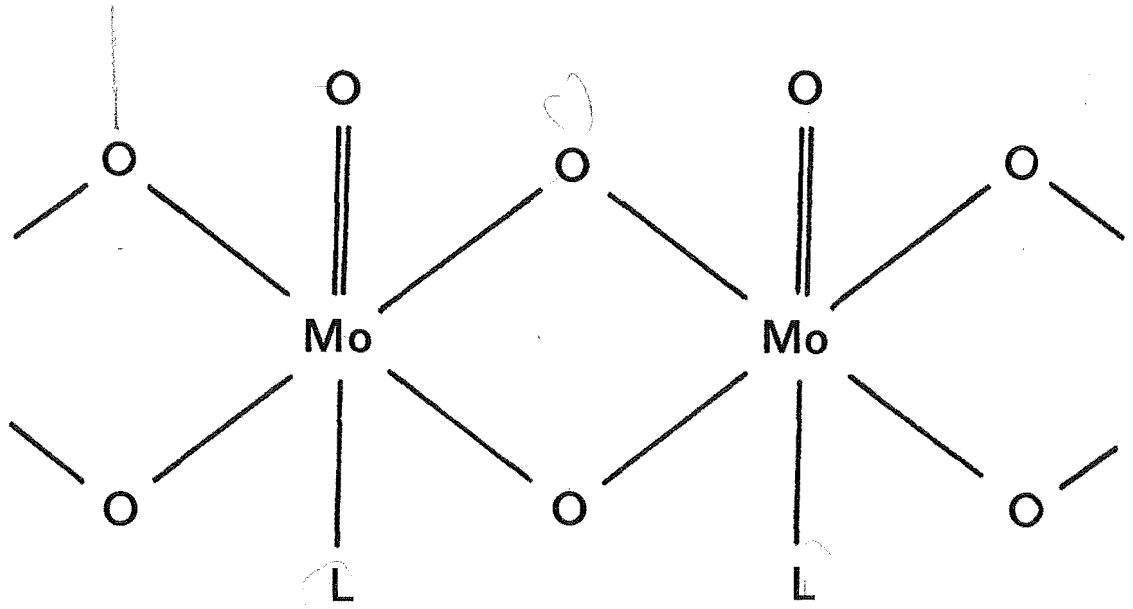


Fig. 3.3(a) Proposed structure for the $[MoO_3L]_n$ complexes

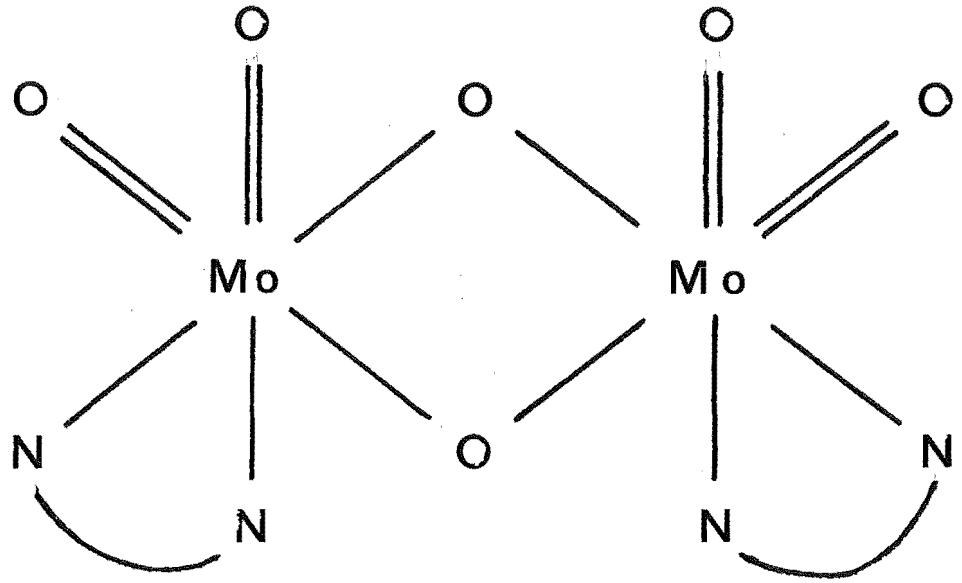


Fig. 3.3(b) Proposed structure for the $Mo_2O_6(bipy)_2$ complex

Table 3.4(a)

Infrared Assignments for $[MoO_3L]$ Compounds

DMF[213]	Molybdenum Complex	Assignment	DMSO[211]	Molybdenum Complex	Assignment	Ph_3PO[212]	Molybdenum Complex	Assignment	Bipy[242]	Molybdenum Complex	Assignment
2940	2945	$\nu^a(CH_3)$	2973		ν(C-H)	3040	3040	ν(C-H)	3086	3098	ν(C-H)
						1594	1594	ν(C-C)			
2928	2930	ν(C-H)	2908		ν(C-H)	1578		ν(C-C)	3078		
						1487	1488	ν(C-C)			
2860		$\nu^s(CH_3)$	1419	1410	δ^a(C-H)	1444	1423	ν(C-C)	3061		
1679vs	1623	ν(C-O), ν(C-N)				1410		combination			
		δ(C-H)	1405			1335		ν(C-C)	3054		
1490		ν(C-N), ν(C-O)				1314	1310	combination			
		δ(C-H)		1318		1281		β(C-H)	1579	1599	
1460		$\delta^a(CH_3)$ out of plane			δ^s(C-H)	1188	1178	β(C-H)			ν(C-N) + ν(C-C)
			1304	1300		1168	1155		1553	1497	
1442		$\delta^a(CH_3)$ in plane				1193	1149	ν(P-O)			
			1016	1028		1122	1115	X sensitive	1448	1479	ring strain
1409	1418	$\delta^s(CH_3)$				1097	1085	combination			
1389	1335	δ(C-H), ν(C-O)	1009	1003	methyl rock	1074	1062	β(C-H)	1410		H bond +
		ν(C-N)				1028	1021	β(C-H)		1309	ring strain
1250	1244	δ^a(C-N-C)	999	993			1006		1248	1241	ring strain
						997	992	p ring			
1095	1119	CH_3 in plane rock		947	ν(Mo-O_t)		984		1210	1221	ring strain

(contd)

Table 3.4(a)

DMF[213]	Molybdenum Complex	Assignment	DMSO[211]	Molybdenum Complex	Assignment	PH_3PO[212]	Molybdenum Complex	Assignment	Bipy[252]	Molybdenum Complex	Assignment
							950	$\nu(Mo\text{-}O_t)$		1170	H in plane bend
1067	1035	CH_3 out of plane rock	1102	915	$\nu(S\text{-}O)$	918	913	$\gamma(C\text{-}H)$	1138	1159	
						860	896	$\gamma(C\text{-}H)$		1108	
	968w			842	$\nu(MoO_2MO)$		878		1090	1088	
						843	851	$\gamma(C\text{-}H)$	1083	1075	ring strain
	953	$\nu(Mo\text{-}O_t)$		799	$\nu(MoO_2Mo)$		820	$\nu(MoO_2Mo)$	1063	1054	+ bend
							783	$\nu(MoO_2Mo)$		1040	
	915w		689	718	$\nu^a(C\text{-}S)$	755	759			1020	H out of plane bend
								$\gamma(C\text{-}H)$			
						750	749		991	991	ring breathing mode
	868	$\nu(MoO_2Mo)$	672	660	$\nu^s(C\text{-}S)$	721	721	X sensitive		910	$\nu(Mo\text{-}O_t)$
							715			880	$\nu(Mo\text{-}O_t)$
866	856	$\delta^s(C\text{-}N\text{-}C)$		555	$\nu(MoO_2Mo)$		689	$\phi(C\text{-}C)$			
							642	$\nu(MoO_2Mo)$		759	$\nu(MoO_2Mo)$
	820	$\nu(MoO_2Mo)$					620	$\alpha(C\text{-}C)$	738		H out of plane bend
							600w			732	$\nu(MoO_2Mo)$
660	741	$\delta(OCN)$				542	552				
							537	X sensitive	651		ring bend
	638	$\nu(MoO_2Mo)$				507	529sh				
										632	$\nu(MoO_2Mo)$

Table 3.4(b)

Frequencies Arising from the Metal-Oxo Core in MoO_3L Compounds

Compound	$\nu(Mo\text{-}O_t)$ cm^{-1}	$\nu(Mo\langle^{O}_{O}\rangle Mo)$		
$[MoO_3Ph_3PO]_n$	950	820	783	642
$[MoO_3DMF]_n$	953	868	820	638
$[MoO_3DMSO]_n$	947	842	799	555
$[MoO_3py]_n$	960	795	708	620
$Mo_2O_6bipy_2$	910,880	759	732	632

3.4 COMPLEXES OF COMPOSITION MoO_2L_2 (L = bidentate ligand monoanion)

The preparation of a number of complexes of the type MoO_2L_2 (HL = ethane-1,2-diol, bis(2-hydroxyethane)ether, pentane-2,4-dione, 8-quinolinol and N,N-diethyldithiocarbamic acid) enabled the examination of their infrared spectra. Although the spectra of the unsymmetrical bidentate chelates are complex it was still possible to distinguish the metal sensitive infrared modes (see table 3.5).

Comparison of the spectra of the symmetrical chelate rings (from S,S and O,O ligands diethyldithiocarbamate and pentane-2,4-dione) with those of the ligands indicated that the metal oxygen and metal sulphur stretching frequencies were at 452, 405 cm^{-1} and 353 cm^{-1} respectively. This latter assignment is not in agreement with that of Larson and Moore[217]. However, on examination of a series of complexes of N,N-diethyldithiocarbamate with different metal ions it was noticed that the band at 490 cm^{-1}, which had been assigned by these authors to the molybdenum sulphur stretching vibration, was not metal sensitive. Also, this assignment is even higher when compared with the values found for the metal oxygen stretching vibration in the pentane-2,4-dione complex, taking into account the greater mass of the sulphur atom. A normal coordinate analysis has been reported on a nickel (II) dimethyldithiocarbamate complex, in which a band at 380cm^{-1} is assigned to the metal-sulphur stretch. All lines of evidence, therefore, point to the assignment of the molybdenum-sulphur stretching frequency to the band at 353 cm^{-1} rather than 490 cm^{-1}.

Table 3.5

Infrared Assignments of MoO_2L_2 Complexes from 600-200 cm^{-1}

Complex	ν(Mo-L) cm^{-1}	$\delta(MoO_2)$ cm^{-1}
$MoO_2(glycol)_2$	587, 568, 532, 520	378
$MoO_2(digol)_2$	592, 582, 557, 553	390
$MoO_2(eta)_2$	552, 525, 270	380sh
$MoO_2(acac)_2$	452, 405	372
$MoO_2(dtc)_2$	353	389
$MoO_2(oxine)_2$	540, 399, 310	364

glycol = 1,2-ethanediolato

digol = bis(2-hydroxyethane)ether

eta = 2 aminoethanolato

acac = pentane-2,4-dionato

dtc = diethyldithiocarbamato

oxine = 8-quinolinolato

For complexes containing ligands with unsymmetrical oxygen donors (ethane-1,2-diol and bis(2-hydroxyethane)ether) having an unsymmetrical chelate ring, a feature common to all infrared spectra was the presence of a structured band envelope centred at 500-550 cm^{-1}. This envelope was at higher frequencies than normally characteristic of molybdenum-ligand (oxygen) stretching frequencies. To demonstrate that this frequency was primarily associated with a metal-ligand stretching vibration involving an anionic ligand, the copper(II) complexes of 2-aminoethanol(LH); $Cu(LH)_2^{2+}$ and CuL_2, were prepared. The complex of the anionic ligand again showed the new high frequency band at 500-550 cm^{-1} while the complex containing the neutral ligand had no peak in this region. It was therefore deduced that the corresponding molybdenum compound is similar with the equivalent metal ligand frequencies in the same region. It is a further inference that the corresponding band in the diol complexes arises from the same structural features, viz a bond formed between the molybdenum and the anionic oxygen of the ligand.

It remains to be remarked that there is a correspondence between molybdenum oxygen bond lengths and molybdenum oxygen stretching frequencies in these complexes (see table 3.6). Thus it would be expected that for the pentane-2,4-donato complex ν(Mo-O) would be intermediate between the corresponding frequencies for $MoO_2Cl_2(DMF)_2$ (ν(Mo-O) at 415, 390 cm^{-1}) and $MoO_2(Bd)_2$ (ν(Mo-O) at ca. 550 cm^{-1}).

The changes in bands associated with the ligand in the free and complexed state give indirect information on the metal ligand interactions. Infrared assignments for the ligands and their complexes are shown in table 3.7. For the ethane-1,2-diolato complex of molybdenum(VI), ν(O-H) is lowered by

Table 3.6

Comparison of Molybdenum Oxygen Bond Lengths with Molybdenum Oxygen Stretching Frequencies

Complex	Mo-O Bond Length (Å)	Mo-O Stretching Frequency (cm^{-1})
$MoO_2(B\bar{d})_2$*	1.935(O^-), 2.284(OH)	550
$MoO_2(acac)_2$	2.08	452,405
$MoO_2Cl_2(DMF)_2$	2.20	415,390

* $B\bar{d}$ = butane-2,3-diolato

Table 3.7

Infrared Spectra of MoO_2L_2 Complexes from 4000-600 cm^{-1}

Glycol(HL)[244]	$MoO_2(L)_2$	Assignment	Diethylene-Glycol(HL)	$MoO_2(L)_2$	Assignment
3333	3030	ν^a(O-H)	3450	3450	ν(O-H)
3155		ν^s(O-H)	2915		ν^a(C-H)
2938		ν^a(C-H)	2860		ν^s(C-H)
2877		ν^s(C-H)	1460		$\delta(CH_2)$
1461		$\delta(CH_2)$	1410		
1332	1357		1358		
	1345				
1294	1312		1320		
	1260	CH_2 deformation		1250	CH_2 deformation
1252	1251		1232	1231	
	1232				
1203	1210		1223		
	1062				
1084			1125	1127	ν(C-O)ether
	1044	ν(C-O)			
1041			1072	1075	
	1018				
			1057	1057	ν(C-O)
	942	ν^s(Mo-O_t)		1025	
	928	ν^a(Mo-O_t)		945	ν^s(Mo-O_t)
882	897	$\rho(CH_2)$		927sh	
	878			915	ν^a(Mo-O_t)
864		ν(C-C)			
	838			897	$\rho(CH_2)$
700	776	δ(COH)		834	ν(C-C)

Table 3.7

Ethanol-amine (LH)	$MoO_2(L^*)_2$	Assignment	Pentane-2,4-dione (HL)	$MoO_2(L)_2$	Assignment
3375	3290		3010	3118	ν(C-H)
3309	3235	ν(N-H)		3006	$\nu(CH_3)$ in plane
3200	3130		2970	2968	$\nu^s(CH_3)$
2950			2920	2918	$\nu(CH_3)$ out of plane
2880		ν(C-H)	1755		
1610	1573	$\delta(NH_2)$	1729		
1470		$\delta(CH_2)$	1708	1584	ν(C=O)
1380	1303	ν(C-N)	1620		
1239	1255	CH_2 deformation		1505	ν(C=C)
1170	1192		1465	1430	$\delta(CH_3)$ out of plane
1100sh	1109	$\delta(NH_2)$	1411	1410	$\delta(CH_3)$ in plane
1080	1069		1363	1355	$\delta^s(CH_3)$
1049	1058		1310	1300	combination
	1042	CH_2 deformation	1250	1260	ν(C=C) + ν(C-CH_3)
	1033			1253	
	1020		1170	1180	δ(C-H) in plane
957w			1155		
	912		1125		
	897	$\nu^s(Mo\text{-}O_t)$	998	1032	CH_3 rock out of plane
	880	$\nu^a(Mo\text{-}O_t)$	960	1020	
				931	$\nu^s(Mo\text{-}O_t)$
875	868sh	ν(C-C)		904	$\nu^a(Mo\text{-}O_t)$
			779	796	δ(CH) out of plane
	628			675	ring deformation
				666	
				648	out of plane deformation

Table 3.7

8-quinolinol (HL)[290,291]	$MoO_2(L)_2$	Assignment	N,N-dimethyl-dithiocarbamate (HL)[292]	$MoO_2(L^*)_2$	Assignment
1585	1589	ν(C=C)+ν(C=N)		2978	
1500	1504			2932	ν(C-H)
1486				2870	
1404	1414			1548	ν^s(C=N)
1381	1319	ν^a(C-O)	1518	1515	ν^a(C=N)
1276	1269		1460	1460	$\delta(CH_3)$
1265	1255		1420	1440	$\delta(CH_3)$
1238	1238	ring vibration + C-H deformation		1385	
1214	1232		1360	1360	CH_2 deformation
1196	1170		1300	1300	
1180			1290	1280	ν^a(C-N)
1165			1254	-	
			1204	1208	
1158			1131	1149	CH_2 deformation
			1094	1097	
1130	1137		1076	1071	
1085	1100	ν^s(C-O)			
1050			1065	1063	ν^s(C-N)
968					
	926	ν^s(Mo-O_t)		1007	ν(C=S)
	916		987	991	
	900	ν^a(Mo-O_t)			
880	887		913	915	CH_3 rock
860	830				
811	811	out of plane bend		910	ν^s(Mo-O_t)
803	796	δ(C-H)			
774	766	δ(C-H)		879	ν^a(Mo-O_t)
737	750	in plane ring deformation			
703		in plane ring deformation	839	844	δ^a(C-C-C)
633	644	in plane ring deformation		789	
			779	775	δ^s(C-C-C)
				599	ring deformation
			560	572	

* diethyl-derivative

300 cm^{-1} relative to the free ligand while the bands arising from ν(C-O) in the ligand show more structure in the complex due to the fact that there are two types of carbon-oxygen bond (C - O → Mo and C - O - Mo).
        |
        H

The spectrum of the 2-aminoethanolato complex shows a considerable change in the 3000-3500 cm^{-1} region as the ligand no longer has an -OH group. Corresponding to a loss of a proton in the complex, the broad band due to the OH group at ca. 3300 cm^{-1} no longer appears and the NH bands move to lower frequencies.

3.4.1 Structure of the Complexes

The structure shown in figure 3.4 was proposed in accord with the fact that molybdenum always arranges its coordination environment so that the weakest donors are trans to the terminal oxygen atoms (see chapter 2). X-ray structure determinations recently reported[43] on the compound MoO_2 (8-quinolinolato)$_2$ and also the butane-2,3-diol structure (see chapter 7) confirm these proposals.

3.5 THE BUTANE-2,3-DIOL COMPLEX OF MOLYBDENUM(VI) AND ITS CHARACTERISATION

The butane-2,3-diol complex just mentioned was prepared in the course of the synthetic work. It was a compound of rather unusual properties and it proved useful as an intermediate in the synthesis of other compounds. The complex had a low melting point (89°C) and a high solubility in all polar organic solvents. In contrast to the related complexes of other diols this complex was not rapidly decomposed by exposure

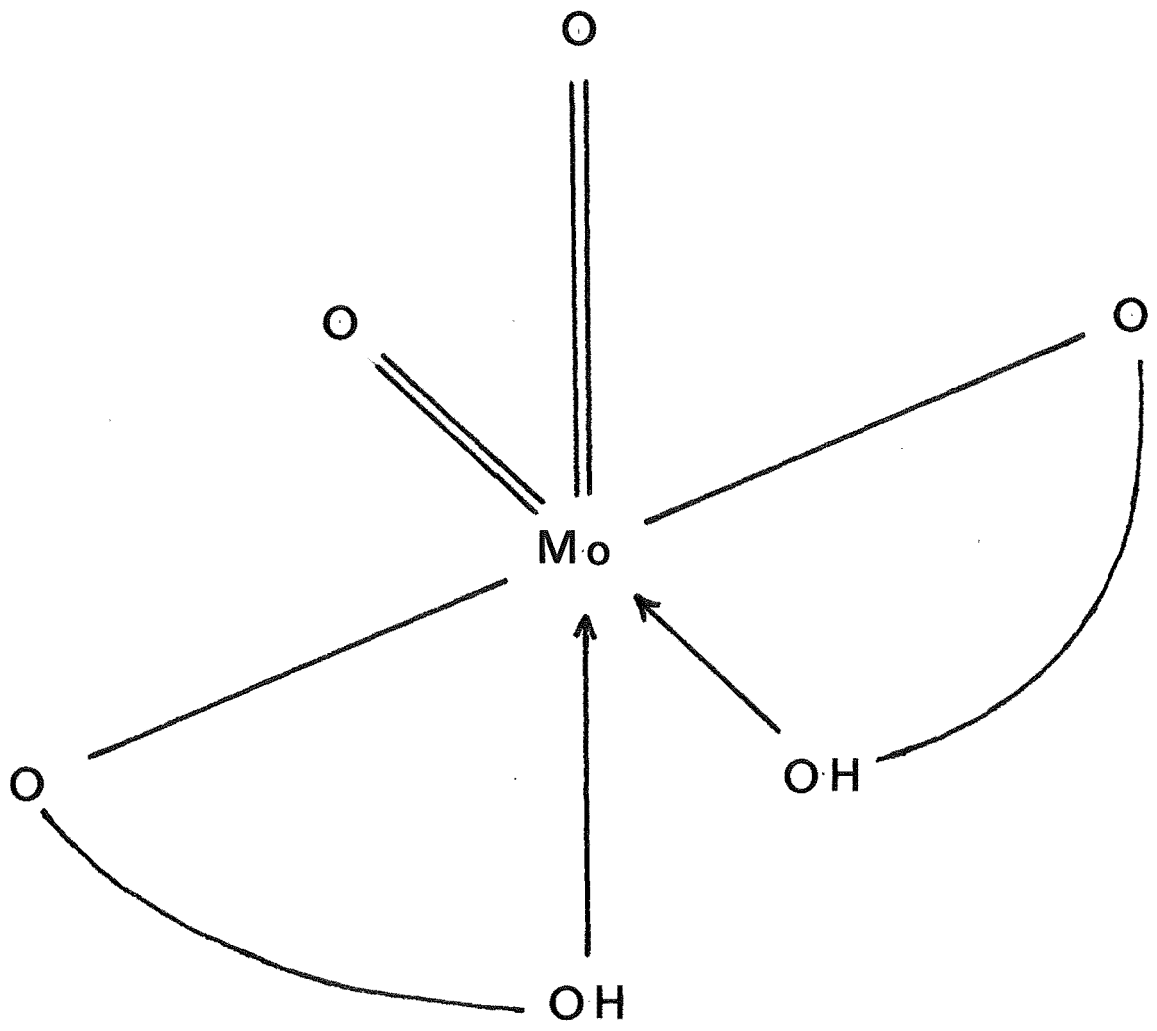


Fig. 3.4 Proposed structure for the MoO_2L_2 complexes

to moist air. However, the structure of the complex proved difficult to deduce from spectroscopic information and the full structure of the compound was only determined finally by X-ray structure analysis (see chapter 7). This structure determination showed that the chelate rings were coordinated to the metal through two different types of oxygen linkage, corresponding to the loss of a proton from one of the hydroxyl groups of each diol molecule.

The complex was obtained by the same type of method used for other diols, i.e. MoO_3 was refluxed for five minutes with liquid ligand and the resulting dark blue suspension filtered. The crystalline compound separated from the filtrate after 2-3 days. The complex analysed to a stoichiometry of $MoO_2 4L$. In acetonitrile at high dilution the complex has a molar conductivity of 43.4 $cm^2.ohm^{-1}$. This is less than that expected for a 1:1 electrolyte (90-130 $cm^2.ohm^{-1}$)[218] but indicates some degree of ionic dissociation in this solvent. A dried fractionated sample of butane-2,3-diol gave a spectrum in solvent of acetone with $\delta(CH_3-)$ at 1.03 and 1.13 Hz, δ(CH-) a multiplet centred at 3.5 Hz, and δ(-OH) a singlet at 3.9 Hz with some structure. The -OH peak was readily identified by its collapse on addition of D_2O (due to the exchange). For a solution (20 mg/0.25 ml) of the diol derivative the spectrum gave δ(-OH) at 3.25 Hz and δ(-CH) a multiplet centred at 3.57 (due to free butanediol) and 4.22 Hz (due to complex) with an integrated intensity ratio of 1:1.6. For a more concentrated solution (32 mg/0.25 ml) δ(-OH) was at 3.33 Hz and δ(-CH-) at 3.56 and 4.17 Hz with the -CH integrated ratios now ca. 1:1.25. Addition of excess butane-2,3-diol to the same caused a marked growth in the -CH- band

at 3.56 Hz (as expected for this is due to free butanediol) and a smaller growth in the band at 4.17 Hz. These observations are all consistent with the existence of two environments for the -CH- groups when the complex is dissolved in acetone. One environment is similar to that for solvent butane-2,3-diol (δ 3.56 Hz) and the other, at lower field, is assumed to represent a -CH- entity adjacent to an -OH group weakly associated with the metal-oxo system. The change in spectra with changing concentration of ligand indicates that the coordinated ligand molecules are labile.

A mass spectrum of the compound showed the presence of a series of peaks (molybdenum has seven main isotopes with relative abundances ranging from 9.6 to 23.0% and spanning mass numbers 92 to 100) centred at 486 m/$\bar{e}$. This molecular ion peak suggests that the complex is undissociated in the gaseous phase.

The infrared spectrum of butane-2,3-diol and its molybdenum complex are presented in figure 3.5. In the range from 650-4000 cm^{-1} the two spectra are identical except for a shift in ν(O-H) from 3370 to 3210 cm^{-1}, in δ(O-H) from 1314 to 1331 cm^{-1}, in ν(C-O) from 1116 to 1107 cm^{-1}; and the appearance of two $\nu(Mo-O_t)$ bands at 948 and 918 cm^{-1}. Also, the band envelopes show little modification in shape such as would occur if the ligands were coordinated as chelates. The conclusion drawn was that the ligands must all be monodentate. The following structure was proposed for the complex (see figure 3.6). In this structure each of the four ligands is coordinated by only one oxygen donor atom to the MoO_2^{2+} centre with two of the ligands having each lost a proton. The two protonated ligands would be expected to be <u>trans</u> to the terminal oxygen

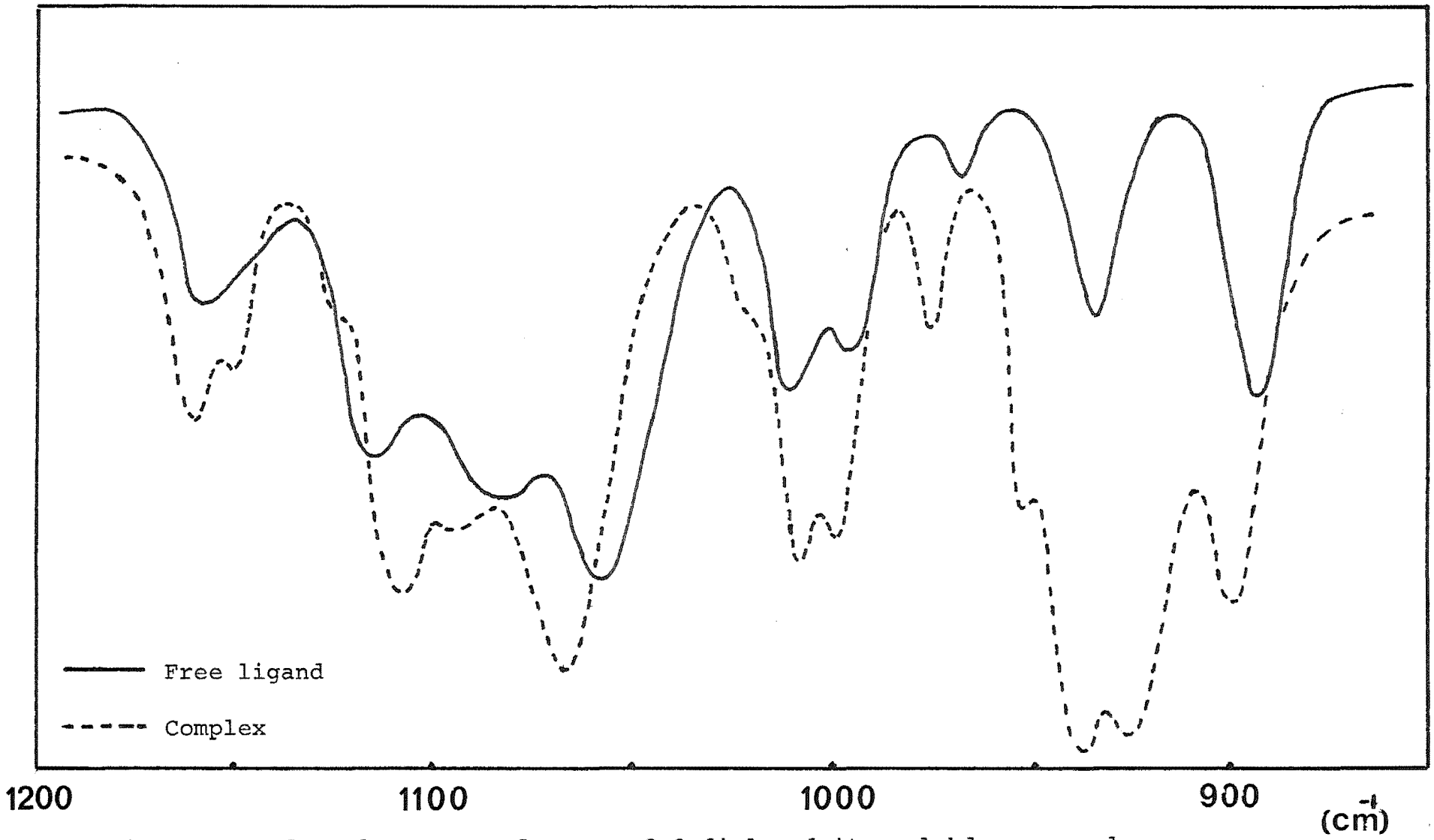


Fig. 3.5 Infrared Spectra of Butane-2,3-diol and its molybdenum complex

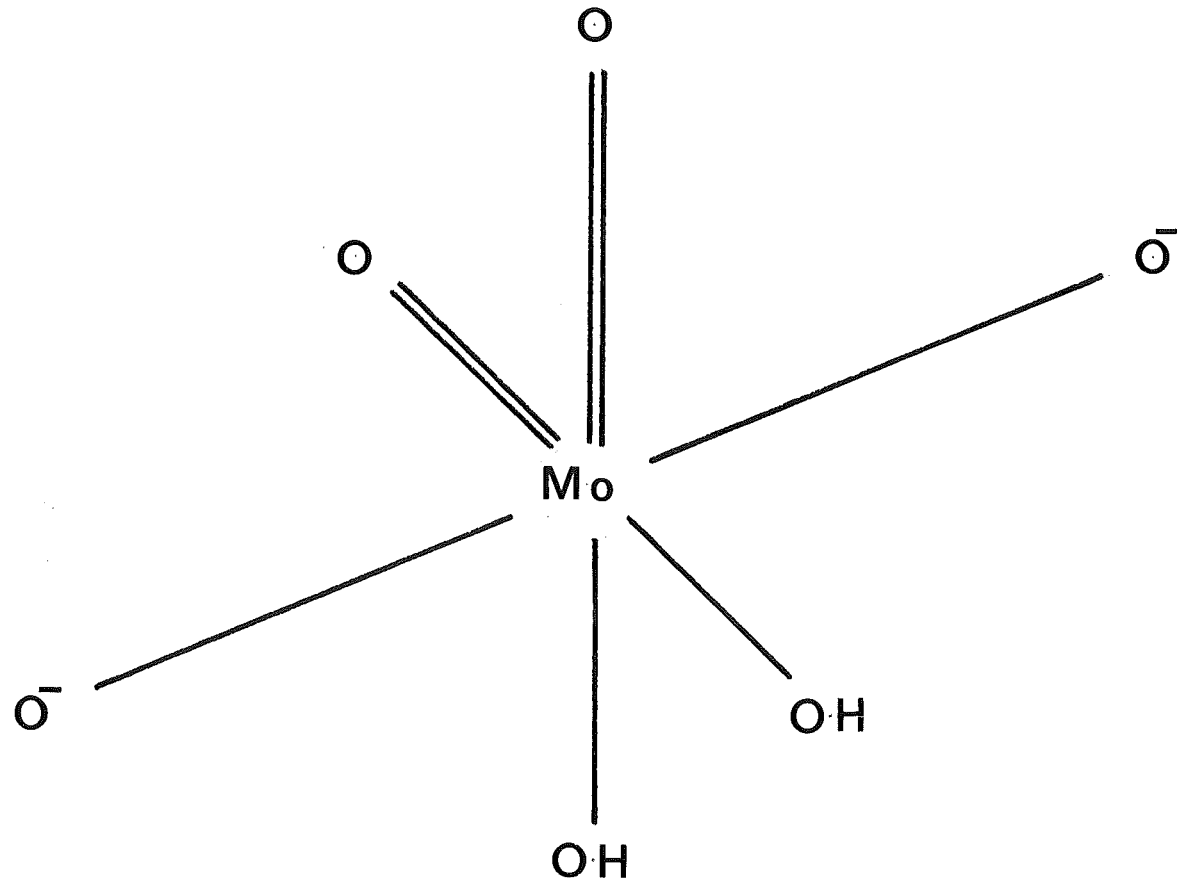


Fig. 3.6 Proposed structure for the Butane-2,3-diol complex of molybdenum.

atoms as these have the weaker -OH donor groups.

This structure can be used to rationalise the evidence. In solution the two ligands trans to the terminal oxygen atoms could dissociate thus explaining both the conductance and NMR results. The ligands are all monodentate and have approximately equivalent environments conforming to the requirements of the infrared spectra.

3.6 PREPARATIVE METHODS IN MOLYBDENUM(V) AND (VI) CHEMISTRY

In reviewing the preparative routes used in molybdenum chemistry the most convenient method of classifying the reactions is in terms of the starting materials and conditions used in the reaction. The best source of molybdenum(VI) for preparative work in aqueous solution is the molybdate ion MoO_4^{2-}. In these cases an aqueous solution of the molybdate is mixed with a solution of the ligand and the pH of the resulting solution adjusted to the appropriate value depending on the oxospecies of molybdenum desired. If a MoO_3 core is required the pH of the solution is adjusted to a value ca. 6-7. A MoO_3 complex of EDTA, $[(MoO_3)_2EDTA]^{4-}$ has been prepared in this way[219]. If a complex containing a MoO_2^{2+} group is required then the pH of resulting solution must be adjusted to a value ca. 1. A complex of diethyldithiocarbamate has been obtained by this method[217]. If the pH of the solution from which the complex is isolated is between 1 and 6-7 then the resulting complex might not necessarily be mononuclear. Depending on the conditions a variety of oxospecies may result, e.g. a complex of the formula $[Mo_4O_{11}(C_4H_3O_5)]^{4-}$ [14] was isolated from a solution of molybdate and malic acid at a pH ca. 3-4. The trioxide MoO_3 has also been used as a source of molybdenum(VI)

in aqueous preparations. Although this compound is insoluble in water, the method involves digesting the trioxide with an aqueous solution of the ligand. A complex of formula MoO_3dien has been prepared in this way[63]. Another way in which complexes have been prepared from MoO_3 involves the refluxing of this compound with liquid ligand. This method has most commonly been employed with protic ligands[220-222] and the complexes so formed involve the loss of a proton, e.g. the preparation of the complex $MoO_2(acac)_2$ [217].

The method which has most commonly been employed in the preparation of adducts of the type $MoO_2X_2L_2$ involves the direct reaction between MoO_2X_2 (X = F, Cl, Br) and the ligand, both dissolved in suitable solvents[20,74,79,191,223-231] (in some cases the ligand itself). However, the necessity of preparing and handling the moisture sensitive MoO_2X_2 compounds is a severe disadvantage of this route.

A more convenient method for the preparation of molybdenum(VI) complexes of the type $MoO_2X_2L_2$ which does not require the initial preparation of the required MoO_2X_2 compound involves the use of a molybdate with either an acid (HX) or acid derivative (RCOX). In the former case molybdate is dissolved in concentrated HX and reacted with the appropriate ligand[232] and in the latter case lead molybdate is reacted with acetyl chloride to produce an acid anhydride adduct of MoO_2Cl_2 in situ. The acid anhydride is then displaced by the required ligand (see next section). Both these methods do not require rigorously dry conditions but the latter method is only applicable for MoO_2Cl_2 adducts.

Another approach which has been employed in the preparation of $MoO_2X_2L_2$ complexes involves the oxidation of lower

valence states of molybdenum in the presence of excess ligand. Commonly used starting materials are $MoCl_5$, $MoOCl_3$ and molybdenum(0) carbonyl complexes. The reaction of $MoCl_5$ with excess triphenylphosphine oxide (Ph_3PO) produced $MoO_2Cl_2(Ph_3PO)_2$[79], while reaction of $MoOCl_3$ with Ph_3AsO yields $MoO_2Cl_2(Ph_3AsO)_2$[233].

Complexes of MoO_2X_2 with monodentate and bidentate ligands can be prepared from molybdenum(0) carbonyl complexes $Mo(CO)_3L_3$ and $Mo(CO)_4L'$ (L = monodentate ligand, L' = bidentate ligand) by their reaction with the halogen X_2 in solution[80,234], e.g. $MoO_2Br_2(Ph_3PO)_2$ from $Mo(CO)_3(Ph_3P)_3$ and MoO_2Cl_2(diphosphine-dioxide)$_2$ from $Mo(CO)_4$(diphosphine). However, these synthetic routes have the disadvantages of contamination of the final product with the corresponding molybdenum(V) adduct and also the need for the preparation of the starting materials.

The major difficulty in preparing molybdenum(VI) compounds has been the lack of suitable starting materials which are easily prepared and handled, soluble and 'stable' in both organic and aqueous solutions. These difficulties are not so marked in the preparative chemistry of molybdenum(V) complexes. The most commonly used starting material is ammonium molybdenyl chloride $(NH_4)_2MoOCl_5$. This compound is soluble in both aqueous and polar organic solvents and is stable to decomposition unless kept in solution at high pH. Compounds prepared with this starting material can contain different oxomolybdenum(V) "cores" depending on the conditions used to isolate the complex. The resulting compounds may contain a single terminal oxygen atom, plus a μ-oxido or a μ,μ'-dioxido bridge depending on the pH of the solution. The

former types of compound are isolated from solutions of lower pH than the dioxobridged species (a monomeric molybdenum(V) complex containing a dioxo group, the first such prepared and characterised, has also been prepared starting with $(NH_4)_2MoOCl_5$ - see chapter 4).

Other starting materials which have been used in the preparation of molybdenum(V) compounds are $MoCl_5$ and $MoOCl_3$. These compounds, however, are difficult to handle and hydrolyse in the presence of moist air. The preparation of some molybdenum(V) compounds has involved the reduction of molybdenum(VI) by the ligand, e.g. the molybdenum(V) cysteine complex $Na_2[Mo_2O_4(cyst)_2]$ [181] and the xanthate complex $Mo_2O_3(xanth)_4$ [9].

3.7 NEW SYNTHETIC ROUTES TO MOLYBDENUM COMPOUNDS

In the course of the preparative work involved in this project some new methods of preparing molybdenum compounds were developed. One compound was found to be particularly useful in the preparation of other compounds. This was the molybdenum butane-2,3-diol compound $MoO_2(C_4H_9O_2)_2.2(C_4H_{10}O_2)$. This compound was found to have a low melting point (89°C) and a high solubility in organic solvents. The coordinated butane-2,3-diol groups were readily displaced by other monodentate and bidentate ligands. Several new compounds were prepared using this method (with Ph_3PO, pyridine, DMF, DMSO, bipyridyl and o-phenanthroline). For those ligands which were insoluble in organic solvents, and whose complexes decomposed in an aqueous environment, complexes could be obtained using the fused molybdenum butane-2,3-diol compound as a reaction medium (a compound with glycine was prepared in this way). This method is particularly important as no other method

provides a synthetic route to complexes whose ligands meet these requirements.

New methods were developed for the syntheses of adducts of MoO_2X_2 (X = Cl,Br) during the course of an infrared investigation of these compounds. The available methods (as summarised above in the introduction to this chapter) were found to be tedious and unreliable as they involved manipulations in a dry atmosphere. It was found that by modifying the preparative method used by Krauss and Huber[223], adducts of MoO_2Cl_2 with Ph_3PO, Me_3AsO, Me_3NO, DMF, DMSO, bipy and ophen, and of MoO_2Br_2 with Ph_3PO were able to be synthesised. The method involved the synthesis of the intermediate $MoO_2Cl_2(Ac_2O)$ (Ac_2O = acetic anhydride) from $PbMoO_4$ plus AcCl (AcCl = acetylchloride) followed by the displacement of Ac_2O by addition of a slight excess of another ligand. This method was found to be particularly suitable for those ligands with low basicities (Ph_3PO, Me_3AsO, Me_3NO, DMF, DMSO) while for the more basic ligands (bipy, pyNO, ophen) the product was contaminated with ligand hydrochloride. However, soxhlet extraction of the crude products into acetone yielded pure compounds in reasonable yields. Using AcBr instead of AcCl enabled the synthesis of the compound $MoO_2Br_2 2Ph_3PO$ but when other ligands were used only intractable oils resulted.

The application of a method[232] used to prepare MoO_2Cl_2 and MoO_2F_2 adducts using HCl and HF to the corresponding MoO_2Br_2 compounds enabled a synthesis of MoO_2Br_2 adducts of DMSO, bipyridyl and ophenanthroline. Molybdic acid was dissolved in a small quantity of concentrated HBr and added to an ethanolic solution of the ligand to yield a crude product. In the case of the bipyridyl and ophenanthroline adducts the

crude product was extracted with acetone to remove the ligand hydrobromide contaminant. The DMSO compound was recrystallised from acetone.

3.8 CONCLUDING REMARKS

Since the aim of this study with model compounds was to investigate the stoichiometry and structure of unknown compounds using infrared spectroscopy as the main tool, it is of interest to see what results have emerged from this work. Firstly it has been possible to fully characterize the infrared spectra of adducts of MoO_2X_2 with simple ligands. Different metal oxo environments have been identified and characterized and ν(Mo-L) assigned for selected MoO_2L_2 complexes. Novel preparative methods have been developed which can be applied in the synthesis of new compounds. The experience gained can now be applied in the investigation of more complex compounds.

CHAPTER 4

STUDIES OF COMPLEXES OF MOLYBDENUM WITH LIGANDS OF BIOLOGICAL INTEREST

4.1 INTRODUCTION

The element molybdenum, in its +5 and +6 oxidation states, plays a crucial role in a number of very important biological processes of which the fixation of atmospheric nitrogen has been of particular interest in recent years. The elucidation of the factors which are important in the chemistry of the interaction of molybdenum with other molecules is particularly relevant in view of the complexity of the biological situation in which such studies are practically impossible. The last chapter described a study of the interaction of molybdenum centres with simple model compounds. The present chapter describes the application of this information in the further study of complexes with ligands of significance within the biological context.

This study falls into three main sections. The first deals with the synthesis, characterisation and infrared spectra of compounds of ethylenediaminetetraacetic acid (EDTA) and other related compounds. These ligands are relevant since they contain a similar combination of functional groups as found in simple amino acids, but with the important difference that the availability of more donor groups within each molecule might promote the formation of polydentate chelates.

The second section deals with the preparation, characterisation and infrared spectra of molybdenum complexes with naturally occurring amino acids. Molybdenum is known to be associated with amino acid residues in enzymes (section 2.2)

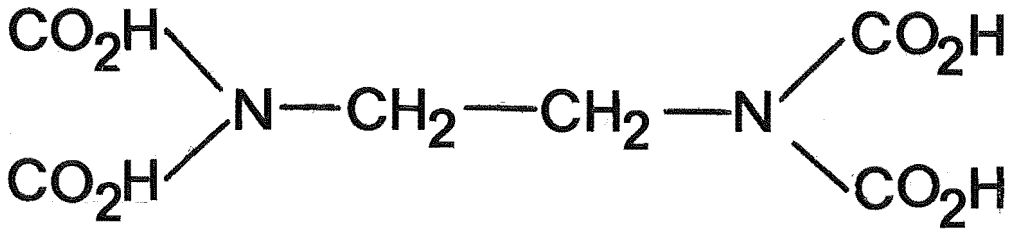
and the preparation of these amino acid complexes should provide evidence on the combinations of functional groups required to promote formation of complexes in aqueous solution.

The third section deals with solution studies made with riboflavin, and simpler molecules structurally related to riboflavin, to determine the most favourable conditions for complex formation. This led on to the isolation of a solid riboflavin derivative.

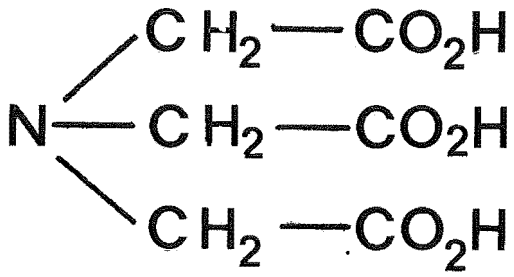
4.2 COMPLEXES OF MOLYBDENUM WITH EDTA AND RELATED LIGANDS

The structural formula for the ligands used in this study are shown in figure 4.1. Most of the previous studies with these ligands have been made on EDTA in aqueous solution. These have included a polarographic study of methods for determining molybdenum[219], measurement of stability constants using NMR techniques[86,235,236], use of circular dichroism, (C.D.) and optical rotatory dispersion (ORD) methods[237], and investigations of the stoichiometry of the interactions between these ligands and molybdenum centres[238]. The infra-red spectra of a number of EDTA complexes (including molybdenum(V) and (VI)) have been reported[239,240] but only those bands arising from the ligand were studied.

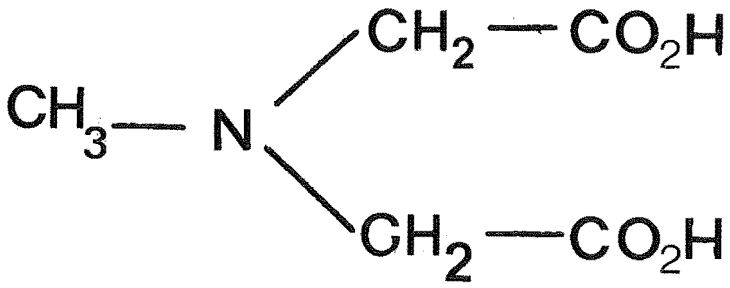
In this present study molybdenum(V) and (VI) complexes of EDTA, IDA, MIDA, NTA and UDA were prepared so that infrared absorptions arising from the molybdenum oxo species could be studied in the presence of a multidentate chelate. Molybdenum(V) complexes of formula $[Mo_2O_4L_2]^{2-}$ were prepared from $(NH_4)_2MoOCl_5$ with the above mentioned ligands (the formula of the EDTA complex being $[Mo_2O_4EDTA]^{2-}$) by mixing aqueous



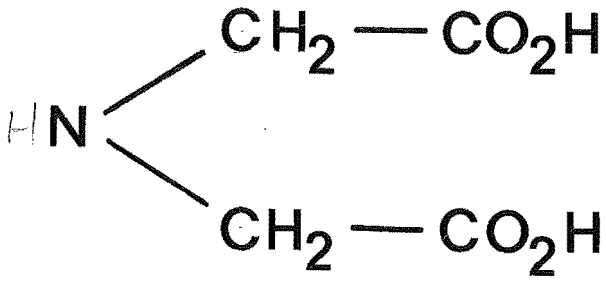
Ethylenediaminetetraacetic acid (EDTA)



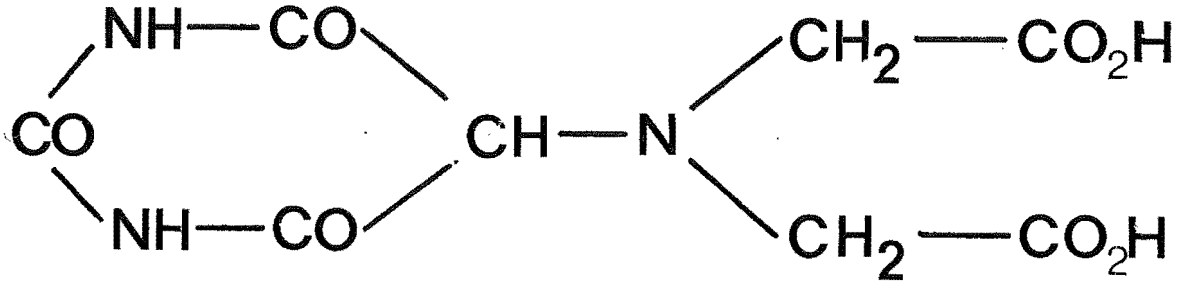
Nitrilotriacetic acid (NTA)



N-methyliminoacetic acid (MIDA)



Methyliminodiacetic acid (IDA)



Uramil-N,N-diacetic acid (UDA)

Fig. 4.1 Structural Formulae for EDTA and Related Ligands

solutions of this compound and the appropriate ligand and adjusting the pH of the resulting solution to ca. 6. Corresponding molybdenum(VI) complexes of formula $[MoO_3L]^{2-}$ were prepared with these same ligands (the formula of the EDTA complex being $[(MoO_2)_2EDTA]^{4-}$) by mixing aqueous solutions of Na_2MoO_4 and ligand and adjusting the pH of the resulting solution to ca. 6.

The complexes were characterised from a consideration of analytical and infrared data. The molybdenum(V) complexes have typically strong infrared absorptions due to vibrations of terminal and bridging oxygen atoms. These frequencies are tabulated in table 4.1. There is only one band in the region expected for a molybdenum terminal oxygen atom stretching frequency (940-980 cm^{-1}) indicating the presence of only a single terminal oxygen atom, whilst there are three bands in the region expected for bridging oxygen atoms (600-850 cm^{-1})[51] indicating the presence of a μ,μ'-dioxobridge. The compounds are thus formulated as $Na_2Mo_2O_4L_2$ and a structural representation is shown in figure 4.2. As can be seen from the diagram the nitrogen donor group is trans to the terminal oxygen atoms. This is in accord with the tendency of molybdenum to arrange its coordination sphere so that the weakest donors occupy a position trans to the terminal oxygen atoms (see chapter 2).

The molybdenum(VI) complexes were characterised in a similar manner to the corresponding molybdenum(V) complexes. However, their infrared spectra showed the presence of one or two bands in the 800-900 cm^{-1} region and in the absence of bands indicating the presence of bridging oxygen atoms the proposed structure for these complexes has a cis trioxo group.

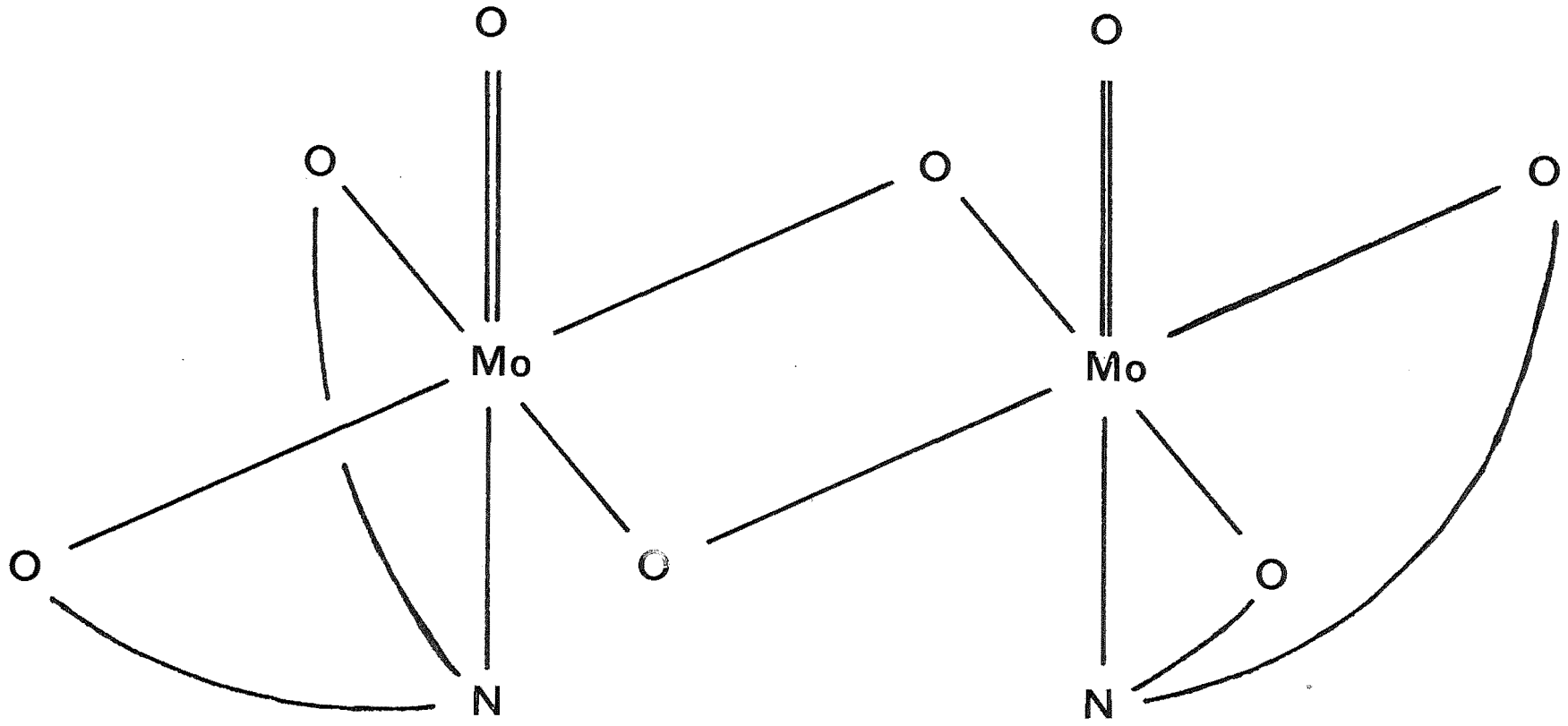


Fig. 4.2 Proposed structure for the $[Mo_2O_4L_2]^{2-}$ Complexes

Table 4.1(a)

Infrared Frequencies of $[Mo_2O_4L_2]^{2-}$ Complexes

Complex	$\nu(Mo\text{-}O_t)$	$\nu(MoO_2Mo)$		
$[Mo_2O_4EDTA]^{2-}$	946	750	718	650
$[Mo_2O_4(UDA)_2]^{2-}$	946	755	722	646
$[Mo_2O_4(IDA)_2]^{2-}$	955	760	730	614sh
$[Mo_2O_4(NTA)_2]^{4-}$	969	755	721	614sh
$[Mo_2O_4MIDA]^{2-}$	956	773	732	616sh
$[Mo_2O_4asp]^{2-}$	936	777	750	656

Table 4.1(b)

Infrared Frequencies of $[MoO_3L]^{2-}$ Complexes

Complex	$\nu^s(Mo\text{-}O_t)$	$\nu^a(Mo\text{-}O_t)$
$[(MoO_3)_2EDTA]^{4-}$	853	835
$[MOoO_3UDA]^{2-}$	850	-
$[MoO_3IDA]^{2-}$	880	-
$[MoO_3NTA]^{3-}$	850	825
$[MoO_3MIDA]^{2-}$	850	828
$[MoO_3asp]^{2-}$		

EDTA = ethylenediamine-N,N,N',N'-tetraacetato

UDA = uramil-N,N-diacetato

IDA = imino-N,N-diacetato

NTA = nitrilo-N,N,N-triacetato

MIDA = N-methyl-N,N-diacetato

asp = aspartato

By altering the conditions involved in the isolation of the complexes, two further complexes of molybdenum(V) and (VI) were obtained with the ligand UDA. The second molybdenum(V) compound was obtained by mixing aqueous solutions of $(NH_4)_2$-$MoOCl_5$ and ligand and adjusting the pH of the resulting solution to ca. 3. The resulting deep yellow solution on standing for 2-3 days deposited yellow crystals. The infrared spectrum showed the presence of two strong sharp bands in the 900-950 cm^{-1} region and no peaks in the 600-850 cm^{-1} region which would be indicative of bridging oxygen atoms. Elemental analyses indicated a formula of $NH_4[MoO_2L].H_2O$ (H_2L = UDA). The absence of bridging oxygen atoms and the presence of a dioxo group indicated that the compound is monomeric and to make up a coordination number of six the ligand must be coordinated through four donor atoms. An X-ray structure analysis of the molybdenum(V) complex (chapter 8) confirmed this proposed structure; this is the first example of a molybdenum(V) monomeric compound containing a dioxo grouping (see chapter 8 for a full analysis of the significance of this result).

A corresponding molybdenum(VI) complex of the same ligand was isolated from an acidified solution of Na_2MoO_4 and ligand. The infrared spectrum of this compound was very similar in both band shape and band position to that found for the molybdenum(V) complex, indicating a similar structure. The infrared spectrum of this complex again showed two peaks in the 900-950 cm^{-1} region indicative of a terminal dioxo grouping and elemental analyses indicated a formulation of MoO_2L (H_2L = UDA). The values of $\nu(Mo\text{-}O_t)$ for the two compounds are; for molybdenum(V) complex 940, 912 cm^{-1} and for molybdenum(V)

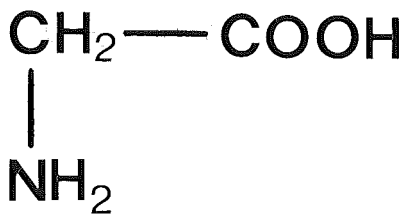
complex 946, 916 cm^{-1}.

The structures of these complexes are particularly relevant as they show that a pyrimidine ring, such as that found in riboflavin, can coordinate to a molybdenum atom if the experimental conditions are appropriate and that there are other donor groups to provide a favourable stereochemical environment. The formation of these different complexes illustrates the importance of utilizing the correct experimental conditions for the isolation of a particular complex.

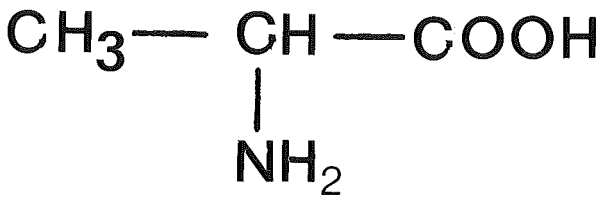
4.3 COMPLEXES OF MOLYBDENUM(V) AND (VI) WITH NATURALLY OCCURRING AMINO ACIDS

The preparation and characterisation of molybdenum(V) and (VI) complexes with amino acids is important in elucidating the coordination requirements of this metal with these ligands. Structural formulae for glycine, alanine and aspartic acid are shown in figure 4.3. It was not possible to obtain glycine complexes from an aqueous medium although a molybdenum(VI) complex could readily be obtained from the reaction of glycine with the butane-2,3-diol intermediate. Failure to obtain a molybdenum(VI) glycine derivative under aqueous conditions is indicative of the complexes rather low stability.

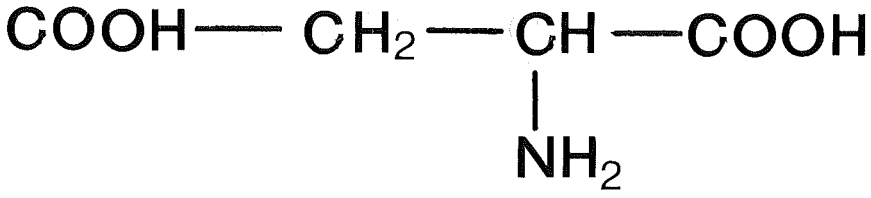
The complex was prepared using the fused molybdenum butanediol complex as reaction medium, extracting the resulting complex from the suspension with methanol and precipitating the complex with ether. The compound was purified by recrystallisation from methanol. The compound was obtained as a pale tan powder and infrared and analytical data showed that the complex could be formulated as $MoO_2 2L$ (LH = glycine). The compound was extremely susceptible to



Glycine



Alanine



Aspartic Acid

Fig. 4.3 Structural Formulae for Three Amino Acids

hydrolysis and all manipulations had to be made in a dry atmosphere. The infrared spectrum showed the presence of two peaks in the 900-950 cm^{-1} region, corresponding to a *cis* dioxo group, and showed the absence of bands due to bridging oxygen atoms. The two $\nu(Mo-O_t)$ modes were found at 935 and 903 cm^{-1}. Thus compound is structurally analogous to the 2-aminoethanol complex described in chapter 3.

As molybdenum is known to arrange its coordination sphere so that the weakest donor atoms are *trans* to the terminal oxygen atoms the glycine molecules are formulated with the nitrogen atoms in these positions while the two oxygen atoms are *trans* to one another. The structure proposed is shown in figure 4.4. Other interesting features in the infrared spectrum are the shift in the carboxylate absorption from *ca.* 1650 cm^{-1} to the region 1705 to 1750 cm^{-1}. There is also a band at 1605 cm^{-1} assigned to $\delta(NH_2)$. The shift in the ν(C-O) can be explained by the fact that molybdenum forms a strong covalent bond with the ligand oxygen atom leaving the other oxygen atom in the COO^- group as almost a pure carbonyl bond (see figure 4.5 for diagrammatic representation of change) with ν(C=O) being found in the carbonyl region of 1700-1750 cm^{-1}.

The method used for the preparation of the molybdenum glycinate complex was applied to the preparation of a similar complex of alanine. However, this was not successful and no characterisable complex could be isolated from the reaction medium.

The preparation of complexes of aspartic acid with molybdenum(V) and (VI) proved more straightforward. In these cases aqueous solutions could be used. A molybdenum(VI) complex was prepared after refluxing MoO_3 with aspartic acid

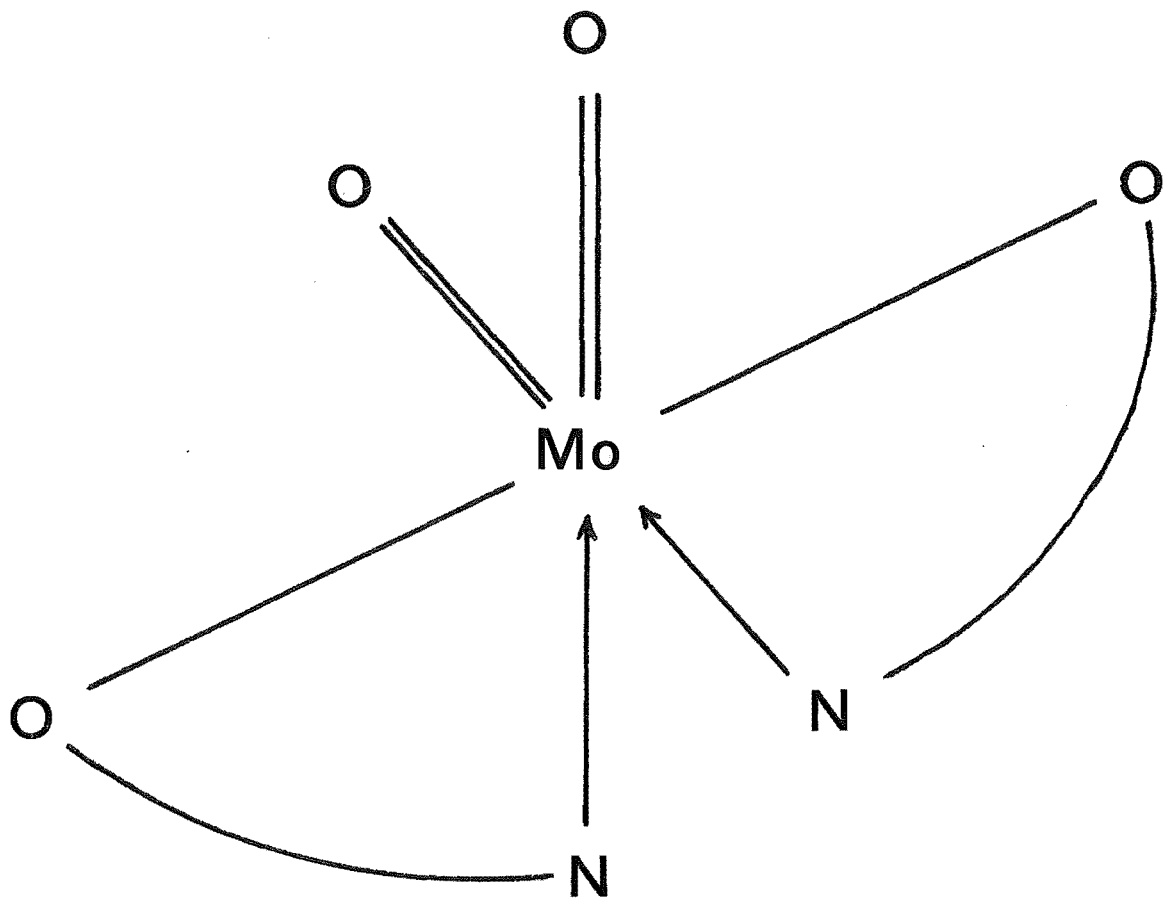
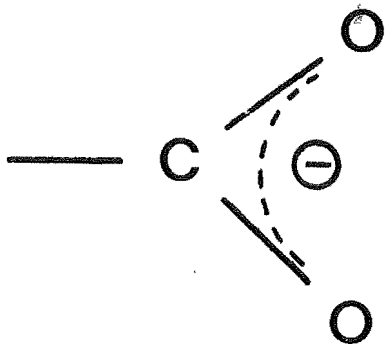
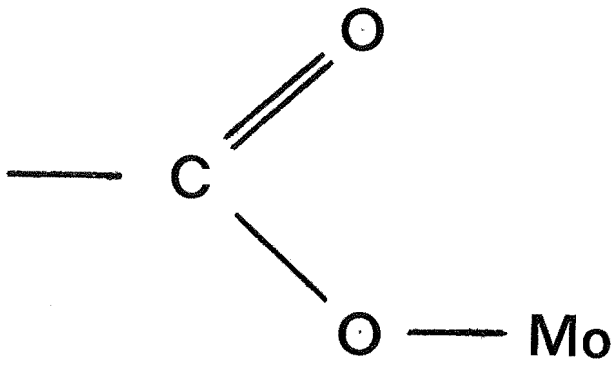


Fig. 4.4 Proposed structure for the Glycine Complex of Molybdenum



Before coordination



After coordination

Fig. 4.5 Modification of COO^- Group on Coordination to a Molybdenum Centre

for 16 hours and then adding two equivalents of KOH. The white crystalline product was obtained by adding ethanol and chilling the solution for 6-7 days. The infrared spectrum of this complex revealed two strong broad bands in the 800-900 cm^{-1} region, at 820 and 860 cm^{-1} indicating, in the absence of other bands related to the presence of bridging oxygen atoms, a MoO_3 core. Elemental analyses established the formula of the complex as $K_2[MoO_3\ asp].2H_2O$. The complex was not subject to hydrolysis in moist air.

A molybdenum(V) complex of aspartic acid was prepared by mixing aqueous solutions of $(NH_4)_2MoOCl_5$ and aspartic acid and adjusting the pH to ca. 6. The complex crystallised from the resulting solution on standing for 2-3 days to yield orange-red crystals. The infrared spectrum showed a single strong absorption at 936 cm^{-1} and three bands at 777, 750 and 656 cm^{-1} indicating the presence of both a single terminal oxygen atom and a μ,μ'-dioxo bridge. Elemental analysis indicated that the formula of this compound was $Na_2[Mo_2O_4asp_2]$. Since the $-NH_2$ group is the weakest donor it is shown trans to the terminal oxygen atom in fig. 4.2. This compound is stable to hydrolysis by moist air. Cysteine and histidine complexes of molybdenum(V) were also prepared in this study but not further investigated as both their preparation and infrared spectra were reported at the same time[180,181].

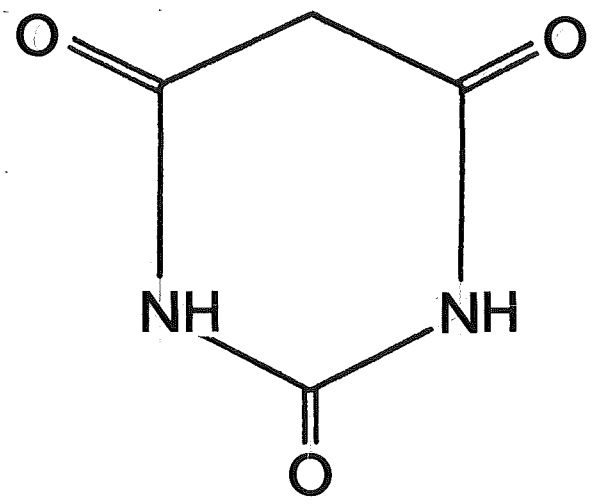
An inference that can be drawn from this preparative work with amino acids is that the combination provided by one $-NH_2$ with a single carboxylate group does not provide stability in aqueous solution and the presence of a third donor group is necessary to ensure this. Complexes of aspartic acid, cysteine and histidine with donor combinations $-NH_2$, $-COO^-$, COO^-; $-NH_2$,

$-COO^-$, S^-; and $-NH_2$, $-COO^-$, =N-; can be prepared from aqueous solution. However, too much weight cannot be placed on these preparative results when considering the role of molybdenum in biological systems where the stability of complex formation is not necessarily an important factor.

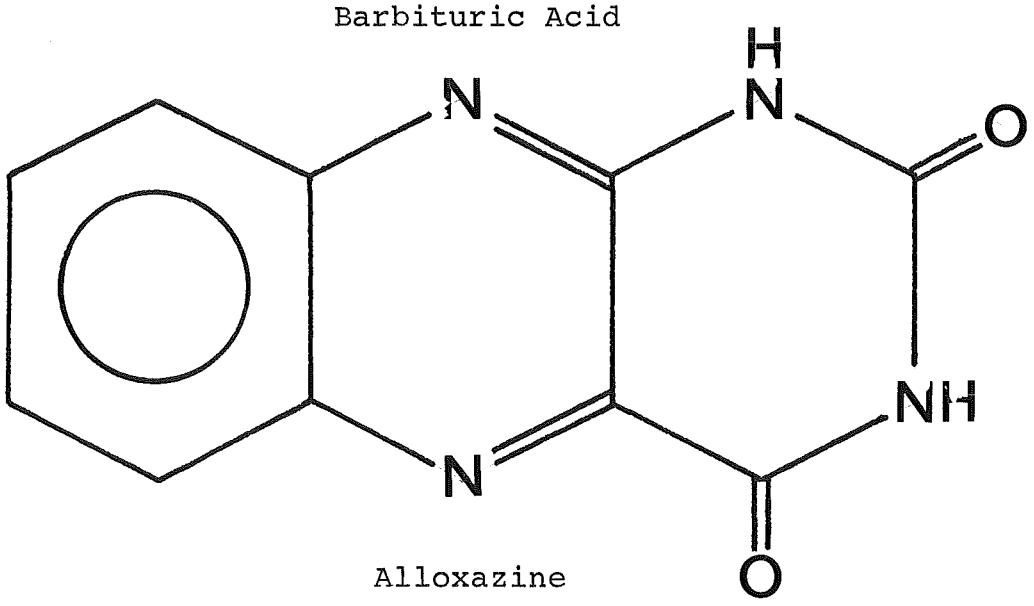
4.4 SOLUTION STUDIES WITH RIBOFLAVIN AND RELATED LIGANDS

The aim of this section was to examine the interaction of copper(II) ions and molybdenum(VI) species with ligands having structures similar to that of components of the riboflavin molecule with the ultimate objective of determining both the stoichiometry of the interaction and the most favourable conditions for the isolation of a molybdenum riboflavin complex. The ligands used in this approach, in addition to the diols, were barbituric acid, alloxazine and riboflavin itself and as can be seen from their structural formulae (fig. 4.6) all contain a pyrimidine ring.

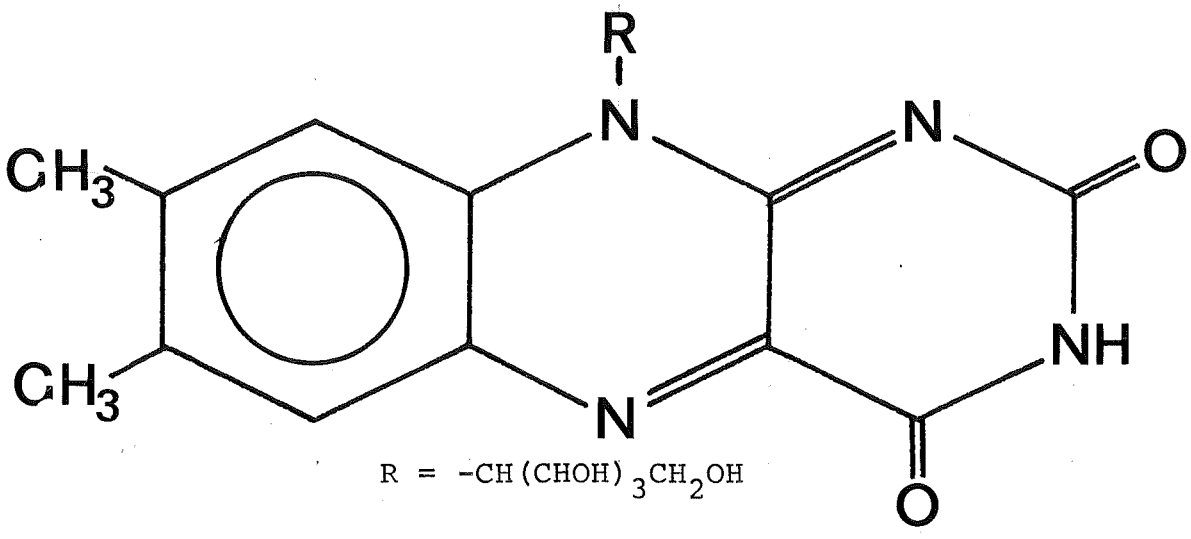
The interaction of barbituric acid with the copper(II) ion was examined spectrophotometrically. For the free acid no evidence for complex formation was found. For the anionic form of the acid, proton loss occurring at the $-CH_2$ group, again no evidence was found for complex formation, although an insoluble green copper salt of the barbiturate ion precipitated from solution. With the dianionic form of the acid, proton loss occurring at an -NH group, evidence for complex formation was found. On addition of a copper(II) solution to a buffered solution of the barbituric acid (carbonate buffer ca. pH 10 was used) a deep blue solution was obtained and examination of



Barbituric Acid



Alloxazine



Riboflavin

Fig. 4.6 Riboflavin and Related Molecules

the visible absorption spectrum showed that the band due to the $Cu(H_2O)_6^{2+}$ ion at 810 mμ had given place to one at 700 mμ. From a Job variation titration the stoichiometry of the interaction was found to be copper: barbiturate ion, 1:2.

The second molecule to be examined in relation to its complexing properties was alloxazine. The spectral investigation was considerably hampered by the low solubility of the compound in all solvents, but although a high degree of accuracy was unobtainable, there was no evidence for complex formation with copper(II) in the pH range 2 to 10.

The third molecule whose behaviour was investigated spectrophotometrically was riboflavin. Again, solubility problems were encountered rendering accurate work difficult, but several useful qualitative observations were obtained. With the riboflavin molecule itself no evidence was found for complex formation; however, for the anionic form of riboflavin (proton loss at N3) there was evidence for complex formation. A Job variation titration showed that the stoichiometry of the interaction was copper(II):riboflavin, 2:1.

4.5 ISOLATION OF A MOLYBDENUM RIBOFLAVIN DERIVATIVE

Chemical studies on the metal coordination chemistry of flavins have been renewed in chapter 2, but it should be emphasised that controversy continues as to the site of the riboflavin metal interaction. The preparation and characterisation of a molybdenum riboflavin derivative therefore becomes all the more important. From the results obtained in the solution studies it was felt that the best chance of success lay with the anionic form of riboflavin, which would

mean working at relatively high pH values. After a number of unsuccessful attempts using aqueous solutions attention was turned to nonaqueous media. The butane-2,3-diol complex of molybdenum(VI) afforded a convenient source of molybdenum(VI) readily soluble in nonaqueous solvents and after some trials of conditions a complex was obtained by refluxing the molybdenum butanediol complex with riboflavin in a 1:1 solution of methanol and pyridine. The purpose of the pyridine was to keep the solution basic and also at the same time hold the molybdenum in solution at this high pH value (the use of a methanolic solution of KOH merely precipitated K_2MoO_4). The complex so prepared appeared to have a stoichiometry of MoO_2R (RH = riboflavin). This complex was able to be isolated from solutions in which the molybdenum riboflavin ratio varied from 1:2 to 2:1. Its infrared spectrum showed the presence of bands due to both MoO_2^{2+} and riboflavin. X-ray powder photographs showed that the complex had diffraction patterns different from those of both starting materials.

The nature of the binding sites proved difficult to elucidate in detail. However, there is no doubt that the ribityl side chain plays a large part in the binding of the molybdenum in view of the known ability of molybdenum to coordinate to polyhydroxy ligands (see chapter 2 for a further discussion of metal binding sites in flavin molecules). Another relevant point is that at the pH at which this reaction was carried out, (ca. 9), sugars have been shown to form their most stable complexes with molybdenum(VI). Further, the infrared spectrum of the molybdenum riboflavin compound showed significant changes in the ν(O-H) region 3000-3500 cm^{-1},

whilst those bands which arise primarily from the isoalloxazine skeleton showed little or no change.

4.6 CONCLUDING REMARKS

Since the reason for undertaking this investigation was to examine the chemistry of molybdenum(V) and (VI) in the light of its function in enzymatic system, it is of interest to see what principles have emerged from the study. Firstly it has been shown that molybdenum forms a wide variety of complexes with ligands which might be found in such naturally occurring molecules as aminoacids and riboflavin . Secondly, it has been shown that in aqueous environments simple amino acid functional groups are not good donor atoms for molybdenum and the presence of a third functional group is necessary for stable complex formation. Thirdly it has been determined that molybdenum forms a complex with riboflavin and that in this compound the main site of the interaction appears to be the ribityl side chain. The possibility remains open that in enzymatic processes the pyrimidine ring plays some part beyond coordination of the molybdenum.

One fundamental question, however, remains to be answered, namely the role of molybdenum in the redox processes which occur in these enzymatic systems. There seems little doubt that the molybdenum(V)-molybdenum(VI) interconversion plays an important part in redox processes in which these enzymatic systems participate. Examination of this role would require a detailed electrochemical investigation of the molybdenum(V)/ molybdenum(VI) redox couple and the way in which it is influenced by coordinated ligands. Some preliminary investigation was carried out in this study but this was not

developed. A survey of the literature showed that previous electrochemical studies on molybdenum have proved difficult to interpret and in most cases reproducible results have not been obtained.

CHAPTER 5

EXPERIMENTAL SECTION

5.1 PREPARATION OF COMPLEXES

5.1.1 Starting Material

Diammonium oxopentachloromolybdate(V) $(NH_4)_2MoOCl_5$

This complex was prepared after the method of Klason[241], stored in a tightly stoppered bottle and recrystallised before use by dissolution in concentrated HCl and precipitated by passing dry HCl gas through the solution. Lustrous green crystals were obtained.

(Found: Mo, 30.7 $(NH_4)_2MoOCl_5$ requires Mo, 31.2%.)

5.1.2 Preparation of Adducts of MoO_2Cl_2 and MoO_2Br_2

These complexes were prepared by two methods. The first method involved the use of $PbMoO_4$ and the second $H_2MoO_4.H_2O$ as starting materials. The two methods were as follows.

Method (a): To a suspension of lead molybdate (5 gms) in 15 mls of solvent (benzene, dichloromethane and acetone were used depending on the requirements of the reaction). A solution of 15 mls of acetylchloride in 15 mls of solvent was added. After the vigorous reaction had ceased (5-7 minutes) the suspension was filtered and to the dark brown filtrate was added a solution containing a slight excess of ligand in a minimum quantity of solvent. The dark brown filtrate changed colour to yellow or light green during addition of the ligand. The resulting solution was placed in a stoppered flask in a cold room (5°C) until the product crystallised from the solution. It was collected by filtration, washed with cold solvent (5 ml),

diethylether (10 ml) and pumped to a hard vacuum.

Method (b): Molybdic acid ($H_2MoO_4.H_2O$) (5g) was dissolved in the minimum quantity of concentrated hydrohalic acid (15-20 ms HCl or HBr as required). A solution containing a slight excess of ligand in a minimum volume of ethanol was then added causing the immediate precipitation of a crude product. This was collected, washed with cold ethanol (5 mls), diethylether (10 mls) and pumped to a hard vacuum.

Compounds prepared by these two methods are listed, with any modifications noted.

Dioxodichlorobis(triphenylphosphineoxide)molybdate(VI)

Method (a) was used with benzene as solvent. The solution turned an orange-yellow colour on addition of ligand. Addition of petroleum ether (50-70°C) was necessary to precipitate the product, which was obtained as yellow crystals.

(Found: C, 57.3; H, 4.00; Cl, 9.5; Mo, 12.7. Calc., for $C_{36}H_{30}Cl_2MoO_4P_2$ C, 57.3; H, 3.85; Cl, 9.4; Mo, 12.7%.)

Dioxodibromobis(triphenylphosphineoxide)molybdate(VI)

Method (a) was used with benzene as solvent and acetyl bromide used instead of acetylchloride. The solution again turned orange-yellow on additon of the ligand. Yellow crystals were obtained.

(Found: C, 51.5; H, 3.78; Br, 19.3; Mo, 10.8. Calc., for $C_{36}H_{30}Br_2MoO_4P_2$ C, 51.3; H, 3.59; Br, 18.9; Mo, 11.4%.)

Dioxodichlorobis(N,N-dimethylformamido)molybdate(VI)

Method (a) was used. The solution turned light green on addition of ligand. Pale green crystals were obtained.

(Found: C, 21.9; H, 4.28; Cl, 20.3; Mo, 27.9. Calc., for $C_6H_{14}Cl_2MoN_2O_4$ C, 20.9; H, 4.06; Cl, 20.6; Mo, 27.8%.)

Dioxodichlorobis(trimethylamine-N-oxide)molybdate(VI)

Method (a) was used. Dichloromethane was used as solvent. The solution turned bright green on addition of ligand. The complex was isolated by addition of diethylether. Green crystals were obtained, mixed with white crystals of ligand hydrochloride. The green crystals were handpicked from the product under a microscope and recrystallised from dichloromethane.

(Found: C, 21.3; H, 5.77; Cl, 20.4; Mo, 27.2. Calc., for $C_6H_{18}Cl_2MoN_2O_4$ C, 20.6; H, 5.19; Cl, 20.4; Mo, 27.4%.)

Dioxodichlorobis(dimethylsulphoxide)molybdate(VI)

Method (a) was used. Dichloromethane was used as solvent. The solution turned pale green on addition of ligand and the white crystalline product was precipitated with diethylether.

(Found: C, 13.8; H, 3.35; Cl, 19.3; Mo, 26.9. Calc., for $C_4H_{12}Cl_2MoO_4S_2$ C, 13.6; H, 3.38; Cl, 19.9; Mo, 27.0%.)

Dioxodibromobis(dimethylsulphoxide)molybdate(VI)

Method (b) was used. The resultant yellow solution was chilled and a crude yellow solid was isolated after 2-3 days. This was collected and recrystallised from acetone to give yellow needles.

(Found: C, 11.0; H, 2.63. Calc., for $C_4H_{12}Br_2MoO_4S_2$ C, 10.8; H, 2.72%.)

Dioxodichlorobis(trimethylarsineoxide)molybdate(VI)

Method (a) was used with dichloromethane as solvent. A light green solution was obtained from which light green crystals were obtained.

(Found: C, 15.2; H, 3.03; Cl, 14.6; Mo, 21.1. Calc., for $C_6H_{18}As_2Cl_2Mo_2O_4$ C, 15.3; H, 3.84; Cl, 15.0; Mo, 20.3%.)

Dioxodichloro(2,2-bipyridine)molybdate(VI)

Method (a) was used with dichloromethane as solvent. An immediate white precipitate was obtained on addition of ligand. This crude product was found to contain considerable quantities of ligand hydrochloride. This impurity was removed by extracting the product with acetone in a sohxlet apparatus followed by a handsorting of the crystals under a microscope and recrystallising from acetone.

(Found: C, 34.1; H, 2.47; N, 8.0. Calc., for $C_{10}H_8Cl_2MoN_2O_2$ C, 33.9; H, 2.26; N, 7.9%.)

Dioxodibromo(2,2'-bipyridine)molybdate(VI)

Method (b) was used and a crude yellow precipitate was obtained on addition of ligand. This was found to be impure and purified by soxhlet extraction into acetone followed by handsorting of the larger orange-red crystals and yellow microcrystalline material. The orange-red crystals were re-crystallised from acetone.

(Found: C, 27.2; H, 2.00; N, 6.4. Calc., for $C_{10}H_8Br_2MoN_2O_2$ C, 27.1; H, 1.82; N, 6.3%.)

Dioxodichloro(o-phenanthroline)molybdate(VI)

Method (a) was used with dichloromethane as solvent. An immediate pale yellow precipitate resulted on addition of ligand. This was purified by soxhlet extraction into acetone followed by handsorting the light green crystals from the product. These were recrystallised from acetone.

(Found: C, 39.3; H, 2.60; N, 7.4. Calc., for $C_{12}H_8Cl_2MoO_2N_2$ C, 38.1; H, 2.17; N, 7.4%.)

Dioxodibromo(o-phenanthroline)molybdate(VI)

Method (b) was used and a yellow product was obtained on addition of ligand. This was extracted into acetone to yield

yellow crystals.

(Found: C, 30.9; H, 1.80; H, 6.1. Calc., for $C_{12}H_8Br_2MoN_2O_2$ C, 30.8; H, 1.73; N, 6.0%.)

Dioxodichlorobis(pyridine-N-oxide)molybdate(VI)

Method (a) was used with dichloromethane as solvent. On mixing the ligand and molybdenum solutions an immediate green product was obtained. Repeated soxhlet extraction into acetone yielded large white crystals.

(Found: C, 31.2; H, 2.81; N, 7.3. Calc., for $C_{10}H_{10}Cl_2MoN_2O_4$ C, 30.9; H, 2.58; N, 7.2%.)

5.1.3 Preparation of MoO_2L_2 Complexes (LH = bidentate ligand)

Dioxobis(ethane-1,2-diolato)molybdate(VI)

This complex was prepared after the method given by Schultheis[220] and a white crystalline product was obtained. All manipulations were carried out in a dry box.

(Found: C, 19.7; H, 5.01; Mo, 3.83. Calc., for $C_4H_{10}MoO_6$ C, 19.7; H, 4.03; Mo, 3.84%.)

Dioxobis(2-aminoethanolato)molybdate(VI)

This complex was prepared by the method given by Schultheis[221] to give a pale tan product. All manipulations involved in the isolation of this complex were carried out in a dry box.

(Found: C, 19.8; H, 5.2; N, 11.2; Mo, 38.6. Calc., for $C_4H_{12}MoN_2O_4$ C, 19.4; H, 4.9; N, 11.3; Mo, 38.7%.)

Dioxobis(di(2-hydroxyethyl)ether)molybdate(VI)

MoO_3 (5 g) was refluxed with the ligand (50 mls) for five minutes and the resulting blue-black suspension was filtered. A white crystalline product was obtained from the filtrate after 2-3 days.

(Found: C, 28.0; H, 5.41; Mo, 28.3. Calc., for $C_8H_{18}MoO_8$ C, 28.4; H, 5.36; Mo, 28.4%.)

Dioxobis(butane-2,3-diolato)molybdate(VI) dibutane-2,3-diol

MoO_3 (5 g) was refluxed with butane-2,3-diol (1:10) for five minutes. The resulting blue-black suspension was filtered and a white crystalline compound isolated from the filtrate after 2-3 days.

(Found: C, 39.5; H, 7.71; Mo, 19.4. Calc., for $C_{16}H_{38}MoO_{10}$ C, 39.5; H, 7.82; Mo, 19.7%.)

Dioxobis(pentane-2,4-dionato)molybdate(VI)

This compound was prepared after the method given by Schulteis[222]. A pale yellow powder was obtained.

(Found: C, 36.5; H, 4.75; Mo, 29.1. Calc., for $C_{10}H_{14}MoO_6$ C, 36.8; H, 4.33; Mo, 29.4%.)

Dioxobis(N,N-diethyldithiocarbamato)molybdate(VI)

This compound was prepared by a previously reported method[217] and the crude material so obtained was recrystallised from benzene to give red crystals which when crushed gave a yellow powder.

(Found: C, 28.6; H, 4.89; S, 30.1; Mo, 22.5. Calc., for $C_{10}H_{20}MoN_2O_2S_4$ C, 28.3; H, 4.75; S, 30.2; Mo, 22.6%.)

Dioxobis(8-quinolinolato)molybdate(VI)

Solutions of sodium molybdate (5 g) and slight excess of 8-quinolinol in water mixed and resulting yellow precipitate was collected, washed with ethanol and diethylether and pumped to a hard vacuum.

(Found: C, 51.5; H, 2.89; N, 6.8; Mo, 23.0. Calc., for $C_{18}H_{12}MoN_2O_4$ C, 51.8; H, 2.98; N, 6.7; Mo, 23.0%.)

5.1.4 Preparation of MoO_3L Complexes (L = monodentate ligand)

Catena-μ,μ-dioxidooxo(N,N-dimethylformamide)molybdate(VI)

Molybdenum trioxide (5 g) was suspended in N,N-dimethylformamide (DMF) (50 ml) and refluxed for four hours. The colour of the solution changed from colourless to deep yellow-brown. The solution was filtered and placed in a stoppered flask in a cold room for 3-4 days during which time a brown crystalline solid was deposited. This was collected, washed with ethanol and diethylether and dried to a hard vacuum. (Found C, 16.6; H, 3.21; N, 6.5; Mo, 44.6. Calc., for $C_2H_7MoNO_4$ C, 16.6; H, 3.25; N, 6.5; Mo, 44.3%.)

Catena-μ,μ-dioxidooxopyridinemolybdate(VI)

Molybdenum-butanediol (5 g) was refluxed with a 1:1 methanol/pyridine solution for 3-4 hours. A red brown crystalline precipitate was deposited during this time and was collected, washed with ethanol and diethylether and pumped to a hard vacuum.

(Found: C, 27.2; H, 2.23; N, 6.3; Mo, 42.9. Calc., for $C_5H_5MoNO_3$ C, 27.6; H, 2.26; N, 6.3; Mo, 43.0%.)

Catena-μ,μ-dioxidooxodimethylsulphoxidemolybdate(VI)

MoO_3 (5 g) was suspended in dimethylsulphoxide (50 ml) (DMSO) and refluxed for 3-4 hours. After filtration a deep yellow solution was obtained, from which a white precipitate was obtained on addition of ethanol. The complex was washed with ethanol and diethylether and vacuum dried.

(Found: C, 11.1; H, 2.71; Mo, 43.0. Calc., for $C_2H_6MoO_3S$ C, 10.8; H, 2.70; Mo, 43.2%.)

Catena-μ,μ-dioxidooxotriphenylphosphinoxidemolybdate(VI)

Molybdenum butanediol complex (5 g) was dissolved in dichloromethane (15 mls) and added to a slight excess of tri-

phenylphosphineoxide in dichloromethane (15 mls) and the solution reduced in volume until a yellow crystalline precipitate was obtained. This was collected, washed with diethylether and vacuum dried.

(Found: C, 50.6; H, 3.68; Mo, 22.0. Calc., for $C_{18}H_{15}MoO_4P$ C, 51.1; H, 3.55; Mo, 22.7%.)

μ,μ-dioxidodioxobis(bipyridine)molybdenum(VI)

Molybdenum-butanediol (5 g) was dissolved in dichloromethane (15 mls) and added to a solution containing a slight excess of bipyridine in dichloromethane (15 mls). A pale pink precipitate separated out, was collected, washed with ethanol and diethylether and vacuum dried.

(Found: C, 41.0; H, 2.68; N, 8.79; Mo, 34.2. Calc., for $C_{20}H_{10}Mo_2N_4O_6$ C, 40.1; H, 2.67; N, 9.3; Mo, 32.4%.)

5.1.5 Preparation of Complexes with EDTA and Related Ligands

Disodium-μ,μ-dioxidodioxo-μ-ethylenediamine-N,N,N',N'-tetraacetodimolybdate(V) monohydrate

$(NH_4)_2MoOCl_5$ (5 g) was dissolved in ethanol (20 mls) and mixed with a solution containing a slight excess of EDTA in ethanol (20 mls). The pH of the resulting solution was increased by the addition of small portions of an ethanolic solution of sodium hydroxide until an approximately neutral solution was obtained. The resulting deep red solution was placed in a stoppered flask in a cold room for 3-4 days when red crystals separated out. These were collected, recrystallised from H_2O/ethanol and vacuum dried.

(Found: C, 20.5; H, 2.33; N, 4.6; Mo, 31.5. Calc., for $C_{10}H_{14}Mo_2N_2Na_2N_2O_{13}$ C, 19.9; H, 2.33; N, 4.6; Mo, 31.6%.)

Disodium-μ,μ-dioxidodioxobis(uramil-N,N-diacetato)dimolybdate-(V) hexahydrate

$(NH_4)_2MoOCl_5$ (5 mmol) and UDA (5 mmol) were crushed together in a small beaker and H_2O (10 ml) was added. The pH of the resulting solution was adjusted to ca. 6 with a 5% aqueous solution of sodium hydroxide. A crimson red solution was obtained, which was evaporated to ca. 50 mls and 150 mls of ethanol was added. After storing in a cold room for 2-3 days crimson red crystals separated out, were collected, recrystallised from water/ethanol and vacuum dried.
(Found: C, 20.5; H, 2.56; N, 9.2; Mo, 20.7. Calc., for $C_{16}H_{26}MoN_6Na_2O_{24}$ C, 20.8; H, 2.82; N, 9.1; Mo, 20.8%.)

Disodium-μ,μ-dioxidodioxobis(iminodiacetato)dimolybdate(V) hexahydrate

The method used was the same as for the UDA complex. On addition of ethanol an orange-red oil separated from the solution. The above liquid was decanted, 2-propanol added and beaker scratched until the oil crystallised. The complex was recrystallised from water. Orange-red crystals were obtained.
(Found: C, 14.5; H, 3.28; N, 4.0; Mo, 28.4. Calc., for $C_8H_{22}Mo_2N_2Na_2O_{18}$ C, 14.3; H, 3.28; N, 4.2; Mo, 28.6%.)

Disodium-μ,μ-dioxidodioxobis(N-methyliminodiacetato)dimolybdate(V) hexahydrate

The same method was used as for the preparation of the IDA complex and orange-red crystals were obtained.
(Found: C, 17.3; H, 3.78; N, 4.0; Mo, 27.6. Calc., for $C_{10}H_{28}Mo_2N_2Na_2$ C, 17.2; H, 3.72; N, 4.0; Mo, 27.5%.)

Tetrasodium-μ,μ-dioxidodioxobis(nitrilotriacetato)dimolybdate(V) monohydrate

Method used was the same as that for the IDA complex. Orange needles were obtained.

(Found: C, 19.2; H, 2.07; N, 3.7; Mo, 25.8. Calc., for $C_{12}H_{14}Mo_2N_2Na_4O_{17}$ C, 19.4; H, 1.89; N, 3.8; Mo, 25.9%.)

Tetrasodiumhexaoxo-μ-ethylenediamine-N,N,N',N'-tetraacetato-dimolybdate(VI) octahydrate

Na_2MoO_4 (5 mmol) and EDTA (5 mmol) were dissolved in H_2O (50 ml) and the pH of the resulting solution was adjusted with a 5% aqueous sodium hydroxide solution to ca. 6. The volume of the resulting solution was reduced to ca. 50 mls and ethanol (150 ml) added. Solution placed in cold room for 2-3 days. White needles were obtained which were recrystallised from H_2O/ethanol.

(Found: C, 14.5; H, 3.63; N, 3.4; Mo, 22.5; Na, 11.7. Calc., for $C_{10}H_{28}Mo_2N_2Na_4O_{22}$ C, 14.8; H, 3.44; N, 3.4; Mo, 23.6; Na, 11.3%.)

Disodiumtrioxouramil-N,N-diacetatomolybdate(VI) tetrahydrate

The method used was the same as that for the EDTA complex. Pale pink crystals were obtained.

(Found: C, 18.4; H, 3.01; N, 8.1; Mo, 18.3, Na, 13.0. Calc. for $C_8H_{15}MoN_3Na_2O_{14}$ C, 18.5; H, 2.89; N,8.1; Mo, 18.3; Na, 12.0%.

Trisodiumtrioxonitrilotriacetatomolybdate(VI) tetrahydrate

A similar method employed as in the preparation of the EDTA complex. White crystals were obtained.

(Found: C, 15.4; H, 2.40; N, 3,1; Mo, 21.4; Na, 16.2. Calc. for $C_6H_{14}MoNNa_3O_{13}$ C, 16.2; H, 31.6; N, 3.2; Mo, 21.7; Na, 15.6%.

Disodiumtrioxo-N-methyliminodiacetatomolybdate(VI) dihydrate

Similar method employed to that used for preparation of the EDTA complex. White crystals were obtained. (Found: C, 15.7; H, 2.97; N, 3.7; Mo, 26.3; Na, 11.9. Calc. for $C_5H_{11}MoNNa_2O_9$ C, 16.2; H, 2.96; N, 3.8; Mo, 25.9; Na, 21.4%.)

Ammoniumdioxouramil-N,N-diacetatomolybdate(V) monohydrate

$(NH_4)_2MoOCl_5$ (5 mmol) and UDA (5 mmol) were mixed and dissolved in H_2O (10 ml). The pH of the resulting solution was adjusted to ca. 6 with a dilute solution of ammonia. The resulting deep yellow-brown solution was set aside to crystallise. After 5-6 days yellow crystals separated out. (Found: C, 22.6; H, 2.81; N, 13.3; Mo, 22.8. $C_8H_{13}MoN_4O_{10}$ C, 22.8; H, 3.09; N, 13.3; Mo, 22.8%.)

Dioxouramil-N,N-diacetatomolybdate(VI) dihydrate

Solutions of Na_2MoO_4 (5 mmol) and UDA (5 mmol) in H_2O (15 mls) were mixed and the pH adjusted to ca. 1 with dilute HCl. The resulting deep yellow solution was reduced to small volume (10 mls) and set aside to crystallise. Yellow needles appeared in clusters after 10 days. (Found: C, 22.5; H, 2.59; N, 9.9; Mo, 23.1. Calc. for $C_8H_{11}MoN_3O_{11}$ C, 22.8; H, 2.61; N, 10.0; Mo, 22.8%.)

5.1.6 Preparation of Amino Acid Complexes of Molybdenum

Dioxobis(glycinato)molybdenum(VI)

Glycine (2 g) and molybdenum butanediol complex (10 g) were placed in a stoppered quickfit flask and held at 100°C for 6 hours. The flask was opened and extracted four times with dry methanol (20 ml) and these extracts were quickly transferred to a dry box. Sufficient quantity of diethylether was added to precipitate the yellow product. This was recrystallised from methanol.

(Found: C, 17.8; H, 3.13; N, 10.1; Mo, 34.8. Calc., for $C_4H_8MoN_2O_6$ C, 17.3; H, 3.62; N, 10.1; Mo, 34.1%.)

Dipotassiumtrioxoaspartatomolybdate(VI) dihydrate

MoO_3 (5 g) was refluxed with a slight excess of aspartic acid in H_2O (50 ml) for 16 hours. Then KOH (2 g) and ethanol (150 ml) were added and solution placed in a cold room for 3-4 days. Translucent plate-like crystals were obtained.
(Found: C, 12.5; H, 2.41; N, 3.6; Mo, 24.5. Calc., for $C_3H_7K_2MoNO_{11}$ C, 12.4; H, 2.32; N, 3.6; Mo, 24.7%.)

Disodium-μ,μ-dioxidodioxobis(aspartato)dimolybdate(V) dihydrate

$(NH_4)_2MoOCl_5$ (5 g) were dissolved in the minimum quantity of H_2O and added to a slight excess of aspartic acid dissolved in a minimum quantity of H_2O. Sufficient quantity of a 5% aqueous sodium hydroxide solution was added to raise the pH of the solution to ca. 6. The orange-red solution was placed in a cold room for 5-6 days and orange crystals separated out which were collected, washed with ethanol and vacuum dried.
(Found: C, 12.4; H, 1.68; N, 4.8; Mo, 33.7. Calc., for $C_6H_{10}Mo_2N_2Na_2O_{14}$ C, 12.6; H, 1.75; N, 4.9; Mo. 33.6%.)

Molybdenum Complex of Riboflavin

10 mM of riboflavine were dissolved in a 1:1 mixture of methanol and pyridine (250 ml) and the molybdenum butanediol complex (10 mmol) was added. Refluxing was continued for one hour and then the product was precipitated with diethylether. An orange-red powder was obtained.
(Found: C, 40.0; H, 3.90; Mo, 18.9. Calc., for $C_{17}H_{19}MoN_4O_8$ C, 40.5; H, 4.00; Mo, 19.1%.)

5.2 ANALYSES

Carbon, hydrogen, nitrogen, sulphur and sodium analyses were carried out at the Microanalytical Laboratory, University of Otago. Molybdenum was determined by an ignition method wherever possible. This involved the ignition of the complex to MoO_3 in a muffle furnace thermostated to $530^{\circ}\pm10^{\circ}C$. Compounds containing cations (such as sodium and potassium ions), phosphorus or halides had to be analysed by a gravimetric procedure with 8-quinolinol as outlined in Vogel[245], after first decomposing the complexes in hot aqueous alkali. Sodium and potassium were determined by a flame photometric procedure as outlined in Vogel[246]. Halide (Br and Cl) analyses were carried out by the Volhard method[247] after the complexes had first been digested with a hot concentrated solution of A.R. KOH.

5.3 INFRARED SPECTRA

Infrared spectra were recorded in the range 4000-400 cm^{-1} on a Perkin Elmer 337 spectrophotometer or a Shimadzu IR-27 G spectrophotometer calibrated with polystyrene. Either nujol mulls with KBr plates or KBr discs were used. Spectra were recorded in the range 500-200 cm^{-1} on a Grubb-Parsons DM4 spectrophotometer, calibrated with water vapour. Nujol mulls were prepared and supported either between CsI plates or on polythene discs. Spectra in the range 400-40 cm^{-1} were obtained by use of a R.I.I.C. Fourier Spectrophotometer FS-720 producing an interferogram which yielded the absorption spectrum after application of a Fourier Transform program (R.I.I.C.) via an IBM 360/44 computer (accuracy ±2 cm^{-1}).

5.4 RAMAN SPECTRA

Raman spectra, on selected samples, were recorded on the Physics Department instrument. The author is grateful to Mr A.M. Greenaway (Chemistry Ph.D. Student) who recorded these spectra.

5.5 ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA

Ultraviolet and visible absorption spectra for solutions were obtained with a Shimadzu MPS-50L spectrophotometer using matched 1 cm quartz cells. Spectra were obtained from solid samples by using the standard reflectance attachment for this instrument.

5.6 NUCLEAR MAGNETIC RESONANCE (^{1}H) SPECTRA

Nuclear magnetic resonance spectra were recorded on a Varian A60 spectrometer. The author is grateful to Mr T. Andrews who recorded most of these spectra. The spectra were recorded in d_6 acetone, d_3 acetonitrile and d_4 methanol with TMS as internal reference.

5.7 MASS SPECTRA

Mass spectra were recorded on an AEI Model MS902 spectrometer by Mr R. Panckhurst to whom the author is grateful.

5.8 X-RAY POWDER PHOTOGRAPHS

X-ray powder photographs were obtained by use of a Philips 114.83 mm camera with CuKα radiation. Finely ground samples were packed into Lindemann tubes.

5.9 CONDUCTIVITY MEASUREMENTS

Conductivity measurements were made at 25°C, using a Philips PR 9550/01 bridge and a cell with removable dip type platinum electrodes. The cell was calibrated against a standard potassium chloride solution.

5.10 PURIFICATION OF SOLVENTS

Since many of the compounds prepared in this study were susceptible to hydrolysis when in solution it was important that all solvents used were dry.

Ether: Solvent containing ethanol and other impurities was washed with aqueous sodium chloride, dried over calcium chloride and stored over sodium wire.

Ethanol, Methanol: dried by the method given by Vogel[248] involving treatment with magnesium activated by iodine followed by fractionation. The middle fraction was stored over molecular sieves.

Acetone: AR grade acetone was stored over anhydrous potassium carbonate.

Acetonitrile: distilled from phosphorus pentoxide and fractionated. A constant boiling fraction was stored over molecular sieves.

Dichloromethane: dried over calcium chloride and stored over molecular sieves.

Benzene, Toluene: dried and stored over sodium wire.

Petroleum Ether: dried over calcium chloride and stored over molecular sieves.

5.11 PURIFICATION OF REAGENTS

All ligands used in this study were commercially available or obtained from other workers. Where it was considered necessary they were recrystallised before use. Some hygroscopic ligands (such as pyridine-N-oxide, trimethylamine-N-oxide) were dried by sublimation before use.

5.12 DEHYDRATING AGENT

Triethylorthoformate has been used extensively in this study as a drying agent[249]. This involved the addition of 1-2 ml of this reagent to those solutions where hydrolysis could occur. Dehydration involves the following reaction

$$(C_2H_5O)_3CH + H_2O \rightarrow 2C_2H_5OH + C_2H_5CO_2H.$$

5.13 DRY BOX

A number of preparations required a dry atmosphere and were carried out in a dry box. This had an evacuable entry port which could be flushed with dry air to enable rapid entry and exit from the box. Before use the box was flushed with dry air for 1-2 days and fresh surfaces of P_2O_5 constantly exposed to the atmosphere within the box. Dry reagents and solvents were stored in the box and it was set up so that all manipulations for a reaction could be carried out without needing to open the entry port.

P A R T I I

CRYSTALLOGRAPHIC STUDIES OF MOLYBDENUM COMPLEXES

CHAPTER 6

GENERAL EXPERIMENTAL, SOLUTION AND REFINEMENT PROCEDURES

6.1 INTRODUCTION

The crystal and molecular structures of three compounds are presented in this section. One, ammonium dioxouramil-N,N-diacetatomolybdate(V) monohydrate, is the first molybdenum(V) compound containing a monomeric dioxo grouping which has been fully characterised and this is of prime interest in view of the possibilities inherent in its stereochemistry[37]. The other two structures contain molybdenum(VI) entities. One of these, dioxobis(butane-2,3-diolato)molybdate(VI)di(butane-2,3-diol) contains a molecular grouping which has two ligand (solvate) molecules bound to a central entity by a comprehensive arrangement of hydrogen bonds. The other structure, tripotassiumtrioxonitrilotriacetatomolybdate(VI)monohydrate contains molybdenum in 6-fold coordination with the potentially tetradentate ligand NTA coordinated through only three donor atoms, viz. two oxygen atoms and a nitrogen atom.

The compounds were taken from among a number of complexes which had preliminary crystallographic studies completed and were chosen because of the chemical interest in their structures, the quality of the crystals available and the nature of their space group. The structures were examined either to determine the stereochemistries of the molecules or to confirm the stereochemistries which had been predicted from other physical and chemical investigations. The fact that in some cases, notably that of the molybdenum butanediol complex, these predictions have not been borne out, effectively demonstrates

the importance of the X-ray technique as an integral part of any investigation of molybdenum chemistry. These three complexes were chosen from a total of five compounds on which preliminary studies had been made in view of the interest in their structures. The preliminary studies made on the other two are detailed in section 6.4.

As mentioned in chapter 2 there are a number of general principles involved in the structural chemistry of molybdenum (V) and (VI) complexes. These are the generality of the coordination number of six for all compounds of molybdenum(V) and (VI) (with only two known exceptions[18,19]) and the variety of metal oxo environments encountered. Another important feature which has been found in the stereochemistry of these complexes is the fact that in all cases the ligands are arranged in the coordination sphere so that the weakest donors are trans to the terminal oxygen atom and the next weakest donors are trans to bridging oxygen atoms. It is of interest to see how these principles are borne out in the three structures presented here.

6.2 EXPERIMENTAL PROCEDURES

6.2.1 Primary Crystal Data

As a preliminary to a structure analysis some fundamental crystal data must be determined. Approximate cell constants were obtained from suitable precession and Weissenberg photographs and the possible spacegroups from a consideration of these photographs. The experimental density in each case was determined by a pycnometric method involving mixtures of two miscible liquids in which the compound was insoluble. This mixture was made up so that the compound neither rose nor

fell and the density of the mixture was then determined in a specific gravity bottle against water. An accuracy of 0.5% is usually obtainable by this method.

A crystal suitable for data collection was selected from a consideration of the quality of the reflections on a precession setting photograph and mounted on a glass fibre. Since the compounds chosen for study were stable in air at room temperatures no precautions were taken to protect the crystals from the atmosphere. One of two methods was used to fix the selected crystal on to the glass fibre. Either the crystal was glued with Araldite or fixed to the fibre by Shellac using a soldering technique. Both methods gave good results, but the former method could be used for all crystals although rigidity was only achieved after 3-4 days, while the latter method gave an almost instantaneously rigid mounting but could only be used on those crystals with reasonably high melting points.

6.2.2 Diffractometry and Collection of X-ray Intensities

The machine used for reflection data collection was a Hilger and Watts computer controlled (PDP 8/I with 4K words storage) four circle diffractometer. Practical work on the diffractometer fell into two main sections: first, the determination of crystal orientation and refinement of unit cell and crystal orientation parameters; and second, the measurement of reflection intensities. The selected crystal was mounted on a goniometer head in a random orientation to minimize the incidence of multiple reflection[250].

The orientation of the crystal on the diffractometer was determined from the setting angles of two or more reflections which had been indexed by use of the program MOLASZ[251]

from the precession setting photograph. Unit cell and crystal orientation parameters were refined simultaneously by the method of least squares[252] using as observations the setting angles of up to twelve accurately centred reflections. The procedure by which the reflections were centred was controlled by the computer. The angles varied were ϕ, χ, and 2θ, for the bisecting mode geometry ($\theta = \omega$). The size of the diffracted beam collimator (DBC) used was 3.5 mm, which precluded resolution of the $K\alpha_1$ and $K\alpha_2$ peaks and thus the wavelength used in the subsequent refinement was $K\bar{\alpha}$, the weighted mean of the $K\alpha_1$-$K\alpha_2$ doublet. The refined parameters obtained following least squares treatment of these observations were considered to be satisfactory when the difference between observed and calculated angles for the twelve reflections was less than 0.03° and the esd's* for the orientation parameters were less than 0.01°. This precision was usually readily achieved.

Neither the X-ray tube take off angle (3°) nor source to crystal distance (23 cm) were changed during crystal alignment. Crystal quality was checked both by a determination of crystal mosaicity (expressed as the width (in degrees) at half height), and a consideration of the symmetry of strong low angle reflections recorded with open counter ω scans[253]. As the tube take off angle was fixed at 3° the values for the half heights obtained were larger than those normally obtained at lower take off angles, but observed values of $0.08 - 0.15^{\circ}$ were considered acceptable.

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* Figures quoted in parentheses throughout this thesis are estimated standard deviations (esd's) in the least significant digit, usually derived from the inverse matrix in the nonlinear least squares refinement calculations.

Intensity data were collected by the θ-2θ scan technique under control of the computer. In all cases MoK$\bar{\alpha}$ radiation with a Zr filter was used. The scans were symmetric and centred on the peak position calculated from the wavelength of MoK$\bar{\alpha}$ radiation (0.7107Å). They were composed of steps of 0.02° in 2θ and 0.01° in ω, the minimum the machine allows, and suitable scan widths were determined experimentally for each crystal.

Stationary-crystal, stationary-counter background counts were measured at the beginning and end of each scan, with total background counting time one half the total scan time. The distance from the crystal to the receiving aperture of the DBC was permanently fixed at 23 cm and all intensity data were collected using a 5.0 mm, DBC.

Attenuators were automatically inserted in the primary beam if the scan count per step exceeded 8000 per second. Since, for the data sets involved in three structures, there were a number of attenuated reflections, attenuator factors for each attenuator used were measured at the conclusion of data collection.

6.2.3 Data Processing

The method of data processing was similar to that of Corfield, Doedens and Ibers[284]. Background scattering was considered to be a linear function of θ throughout the scan range, so that

$$I = C - \tfrac{1}{2}(t_c/t_b)(\beta_1+\beta_2) \qquad (1)$$

where C is the scan count, β_1 and β_2 are the first and second background counts, and t_c and t_b are the scan and background counting times. The estimated standard deviation (esd) in

the intensity I was computed as

$$\sigma(I) = [C + \tfrac{1}{4}(t_c/t_b)^2(\beta_1+\beta_2) + (pI)^2]^{\frac{1}{2}}, \qquad (2)$$

where 'p' is a factor introduced to avoid overweighting strong reflections[255]. In all data sets, weights were adjusted so that the function minimised showed the minimum systematic dependence on $|F_o|$, $\sin\theta/\lambda$, and reflection indices[256]. The weights ω were taken as $4F_0^2/[\sigma(F_0)^2]^2$, and were adjusted by varying the value p in the expression for $\sigma(F_0^2)$. Values for p for the butanediol, uramil, and NTA structures were finally set at 0.03, 0.03 and 0.05, respectively, and were determined from an analysis of the agreement between observed and calculated structure factors near the end of each refinement.

In the course of a data collection a number of reflections was observed more than once. This was due to either a machine malfunction or because more than one equivalent member of a form was collected. Values of F^2 for these data were taken as the weighted mean of the individual observations.

Absorption corrections were applied prior to the final refinement using Gaussian integration. Input to the program, DABS,[157] consisted of the indices of the boundary faces of the crystal with perpendicular distances of these faces from an arbitrary origin in the crystal. Checks could be made that the size and shape of the crystal were correctly defined by plotting the calculated points of intersection of all boundary faces and comparing the resulting representation with the shape of the crystal itself. A decrease in the R factor following refinement of only scale and temperature factors was a further check that the absorption corrections were applied in the correct sense. These checks were carried out in all cases as a standard procedure.

6.3 SOLUTION AND REFINEMENT PROCEDURES

The structures described in this thesis were solved by a combination of Patterson and Fourier techniques, and were refined by least-squares methods. These techniques are outlined in this section.

6.3.1 The Patterson Function

All three structures described in this study were solved by inspection of the Patterson syntheses as in all cases the heavy atom vectors due to molybdenum were easily identified. The Patterson function[258], commonly written in Fourier series form as

$$P(u,v,w) = V^{-1} \sum_{h} \sum_{k} \sum_{\ell} |F(hk\ell)|^2 \cos 2\pi(hu + kv + \ell w) \qquad (3)$$

shows maxima corresponding to interatomic vectors between all pairs of atoms at (u+x, v+y, w+z) and (x,y,z) in the unit cell. For a structure containing N atoms per unit cell, the Patterson function will show N^2 peaks, of which N will be vectors of zero length from each atom to itself and will be concentrated as the dominant maximum at $u = v = w = 0$. In all cases the molybdenum vectors were readily identified and no "sharpening" of the Patterson function was required.

6.3.2 Structure Factor Calculations and Least Squares Refinement

Positional and thermal parameters of the atom(s) located by inspection of the Patterson map were refined by the method of least-squares. Refinement proceeded by successive difference electron density maps, to locate remaining non-hydrogen atoms, and least squares cycles.

The general expression for the structure factor may be written as

$$F_c = F_i(S) = \sum^{N} f_i(S).T_i(S).\exp(2\pi iS.r_i) \qquad (4)$$

where $f_i(S)$ is the atomic scattering factor, $T_i(S)$ is a function describing the thermal behaviour of the atomic nucleus, r_i is a vector representing the position of atom i in the unit cell and S is the scattering vector. Structure factor calculations as performed by the program CUCLS[259] use two main approximations, firstly that the atoms are vibrating in a harmonic potential field, either anisotropically (6 parameters per atom) or isotropically (1 parameter per atom), and secondly that tabulated values of atomic scattering factors, calculated for a hypothetical atom in the ground state and with a spherically symmetrical electron density, were used in all cases. Scattering factors used for all non-hydrogen atoms were those of Cromer and Mann[260]. Anomalous dispersion corrections used for the heavier elements were those of Cromer[261]. Scattering factors for the hydrogen atoms were taken from Stewart et al.[262]. Program CUCLS, for structure factor calculation and least squares refinement, contains routines to apply rigorous corrections for the effects of anomalous dispersion (these were written by Ibers and Hamilton[263] and corrections are made to F_c).

Structure factor and refinement calculations for the structures described in this thesis were based on F and the quantity $\Sigma w(|F_0| - |F_c|)^2$ was minimized. Weights were taken as $4F_0^2/\sigma^2(F_0^2)$. The conventional R factor, R_1, and the weighted R factor, R_2, are defined as;

$$R_1 = \Sigma \, ||F_0| - |F_c|| \, / \Sigma |F_0| \qquad (5)$$

and

$$R_2 = (\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2)^{\frac{1}{2}}. \qquad (6)$$

6.3.3 Observed Fourier Synthesis

This may be expressed in the form

$$\rho(x,y,z) = V^{-1} \sum_h \sum_k \sum_\ell F_0 \exp(i\alpha_c) \exp(-2\pi i\delta) \qquad (7)$$

where α_c is the phase predetermined by some method and $\delta = hx + ky + \ell z$. The input data for the Fourier calculations consist of the observed structure factors (F_0) and some source of phases (α_c) for these. In the usual case, the phases are those calculated for a trial structure, e.g. for the butane-diol complex (see chapter 7), phases for F_0 were based on those for F_c calculated on the refined position of the molybdenum atom. The structure was finally solved by calculating the F_0 Fourier in sections and plotting the results on glass plates (via the program CONTOUR)[264] thus reconstructing a three dimensional representation of the observed electron density. From this plot positions for the atoms surrounding molybdenum could be obtained by inspection and the normal difference Fourier-least squares refinement reiteration could be followed.

6.3.4 Difference Fourier Synthesis

This may be expressed as

$$\Delta\rho(x,y,z) = V^{-1} \sum_h \sum_k \sum_\ell (|F_0| - |F_c|) \exp(i\alpha_c) \exp(-2\pi i\delta) \qquad (8)$$

where α_c is the phase of F_c and $\delta = hx + ky + \ell z$. In so far as the phase of F_c is a valid approximation to the phase of F_0 a difference Fourier synthesis represents the difference in

electron density between the actual structure and the model used to calculate F_c. Difference Fourier syntheses were used routinely throughout the structure solving process. All Fourier syntheses for these structures were calculated in three dimensions and the function was evaluated within the unit cell at discrete sampling points arranged in a regular lattice with uniform spacings (usually ca. 0.4Å) between points parallel to each unit cell axis. In most cases Fourier maps were not plotted (with the above mentioned exceptions) as sufficient information could be found from a list of peaks obtained from the map by the Fourier summation program FOURIER[265].

6.4 PRELIMINARY STUDIES ON MOLYBDENUM COMPLEXES

6.4.1 Dioxodichlorobis(triphenylphosphineoxide)molybdenum(VI)

A preliminary study was completed on the above compound to examine the suitability of carrying out a full structural analysis. Well formed golden yellow shiny crystals were obtained from slow evaporation of a dichloromethane solution. Crystal shape approximated that of a truncated rectangular biprism.

Crystallographic Data

$MoC_{36}H_{30}O_4P_2Cl_2$, F.W. = 755 is monoclinic with a = 9.7, b = 10.0, c = 17.8Å, β = 99.1°, U = 1702Å^3; D_m = 1.48(1) g.cm^{-3}, D_c = 1.47 g.cm^{-3}, Z = 2, μ(MoKα) = 6.68 cm^{-1}.

Systematic absences occurred for $ok0$ reflections when k was odd indicating the possible space groups as $P2_1$ or $P2_1/m$. Unit cell dimensions were measured directly from Polaroid precession photographs while the density was determined by the

pycnometric method using the liquids bromobenzene and chlorobenzene for flotation.

The general multiplicities of the indicated space groups $\underline{P}\ 2_{\underline{1}}$ and $\underline{P}\ 2_{\underline{1}}/\underline{m}$ are 2 and 4 respectively. If the space group is $\underline{P}\ 2_1/\underline{m}$ the molybdenum atom must lie on a mirror plane at x, ¼, z since the other special positions all require the molecule to have point group symmetry of $\bar{1}$ (centre of inversion). This is clearly impossible in view of the coordination environment of the molybdenum atom (two ligand oxygen atoms, two chlorine atoms and a cis dioxo group). If the space group is $\underline{P}\ 2_1$, however, there are no symmetry requirements made on the molecule.

In view of the fact that a number of structure analyses had been carried out on adducts of the type $MoO_2X_2 2L$ (X = Cl, Br; L = monodentate aprotic ligand[4,7,190]) it was felt that a full structure analysis was not warranted.

6.4.2 Dipotassiumtrioxoaspartatomolybdenum(VI)dihydrate

A preliminary study was carried out on this compound to establish its suitability for a full structure analysis. There have been several structure analyses of complexes of molybdenum(V) and (VI) with amino acids reported recently and current interest in this field is high[10,18,19,182,185]. Colourless, transparent crystals were obtained from an aqueous solution of the compound to which ethanol had been added. The crystals tended to grow together but when single were square based plates.

Crystallographic Data

$MoC_3H_7O_9NK_2$, F.W. = 375 is orthorhombic with $\underline{a}$ = 11.09, $\underline{b}$ = 11.09, $\underline{c}$ = 9.61Å, $\underline{U}$ = 1192Å^3; $\underline{D}_m$ = 2.12 g.cm^{-3}, $\underline{D}_c$ = 2.12 g.cm^{-3}, z = 4, μ(MoKα) = 11.19 cm^{-1}.

Systematic absences occurred for hoo reflections when h was odd and oko reflections when k was odd uniquely indicating the space group $P_{2_12_12}$. Unit cell dimensions were measured directly from Polaroid precession photographs and Weissenberg wet photographs. The density was determined by the pycnometric method using 1,2-dibromoethane and tetrachloromethane. As the general multiplicity of the indicated space group is 4 there is no symmetry requirement made on the molecule.

During the photography associated with finding the space group a number of anomalies arose. The first of these was associated with difficulty in obtaining a single crystal of suitable qualtiy. On precipitation the crystals tended to grow together in aggregates. Single crystals, when obtained, invariably gave photographs of poor quality. The second difficulty arose in the interpretation of the photographs taken. The lengths of the a and b axes appeared identical but on close examination of precession and Weissenberg photographs the required 4/m symmetry was absent. Therefore the space group had to be orthorhombic.

Although the interest in this complex of a tridentate amino acid must remain high, the unsatisfactory nature of both the crystals and the photography meant that the structure analysis proceeded no further.

CHAPTER 7

THE CRYSTAL AND MOLECULAR STRUCTURE OF $MoO_2(C_4H_9O_2)_2.2(C_4H_{10}O_2)$

7.1 INTRODUCTION

The compound chosen for this analysis was prepared as part of a study of the interaction of molybdenum(VI) with diols. It was immediately observed to possess anomalous properties. It had an abnormally low melting point (89°C) and high solubility in organic solvents. Chemical analyses indicated a metal:ligand ratio of 1:4. Infrared and other physical data suggested that the molecule contained monodentate ligands of which two were bonding through $-O^-$ groups. In view of the fact that molybdenum arranges its coordination sphere so that the weakest donors are *trans* to the terminal oxygen atoms the structure shown in figure 3.6 was proposed.

In view of these chemical anomalies and as no structural work had been published on molybdenum diol complexes it was felt to be of interest to determine the structure of the molecule by X-ray analysis and thus to test the deductions from spectroscopic and other physical evidence.

7.2 EXPERIMENTAL

The compound was prepared as outlined in chapter 5 from MoO_3 and butane-2,3-diol. Clear, transparent crystals with well defined faces were obtained by recrystallising the compound from acetonitrile.

Crystallographic Data

$C_{16}H_{38}O_{10}Mo$, F.W. 486.4 is monoclinic with a = 16.269(5), b = 9.848(5), c = 14.313(5)Å, β = 91.31(5)°; V = 2293Å^3;

$\underline{d}_{obs}$ = 1.410(5) g.cm^{-3}, z = 4, $\underline{d}_{calc}$ = 1.41 g.cm^{-3}; μ(Mo-Kα) = 6.11 cm^{-1}; F(000) = 1024.

Systematic absences occurred for h k o reflections when (h+k) was odd and for h o ℓ reflections when ℓ was odd. Possible space groups were therefore $\underline{C}_{2h}^{6}$ - $\underline{C}$ 2/c or $\underline{C}_{s}^{4}$ - $\underline{C}$ c. Intensity statistics[271] were ambiguous (see table 7.1 for an analysis of the intensity statistics) but the centrosymmetric space group $\underline{C}$ 2/$\underline{c}$ was finally shown to be the correct choice by a subsequent successful solution and refinement of the structure. This space group requires molecular symmetry $\underline{C}_{i}$ - $\bar{1}$ or $\underline{C}_{2}$ - 2.

Unit cell dimensions and their estimated standard deviations (esd's) were obtained by least squares refinement of the setting angles of twelve reflections accurately centred in a 3.5 mm diameter circular receiving aperture in the manner outlined by Busing[266] and adapted to the system used in the Crystallographic Laboratory of the University of Canterbury (see chapter 6 for full details). The experimental density was determined by a pycnometric method using chlorobenzene and bromobenzene for flotation.

Diffraction data were obtained from a crystal whose shape approximated to that of an irregular hexagonal bipyramid with boundary faces defined by the forms {110}, {$\bar{1}\bar{1}$0}, {1$\bar{1}$0},{$\bar{1}$10}, {100}, {$\bar{1}$00}, {001} and {00$\bar{1}$}. Crystal dimensions normal to these faces were 0.09, 0.09, 0.10, 0.10, 0.06, 0.06, 0.15 and 0.15 mm respectively. A preliminary mosaicity check of the crystal showed that the width at half height of intense low angle reflections was acceptably low at 0.15°. Intensity data were recorded as described in chapter 6. Attenuators were automatically inserted in the primary beam if the total scan count per step exceeded 8000/sec. The intensities of three

Table 7.1

Intensity Statistics for the Molybdenum Butanediol Complex

Group	E(1)	E(2)	E(3)	E(4)	Theoretical Centric	Theoretical Noncentric
Mean Mod. E	0.8434	0.8204	0.8630	0.8506	0.7980	0.8860
Mean Mod. E^2	1.0117	0.9643	1.0533	1.0292	1.0000	1.0000
$\frac{1}{\text{Mean Mod. } E^2}$	0.8246	0.8084	0.8470	0.8415	0.9680	0.7360
E > 1.0	40.13	37.57	42.25	40.42	31.73	36.79
E > 1.2	26.61	24.93	29.61	27.92	23.01	23.69
E > 1.4	17.25	15.28	18.93	18.35	16.15	14.09
E > 1.6	9.43	8.70	10.38	9.80	10.96	7.73
E > 1.8	4.46	4.53	4.90	4.61	7.19	3.92
E > 2.0	2.12	1.83	1.97	1.90	4.55	1.83
E > 2.5	0.15	0.07	0.07	0.07	1.24	0.19
E > 3.0	0.0	0.0	0.0	0.0	0.27	0.01

strong reflections well separated in reciprocal space were used as standards and monitored throughout the data collection. These showed no significant variation. In all, 1750 reflections were collected in this way, and after editing[272] and averaging of equivalent forms there was a total of 1368 independent reflections recorded within the range $0 < 2\theta < 43.6^{o}$ of which 245 were considered as unobserved as they had intensities less than $\sigma(I)$.

Absorption corrections[257] were applied before the final refinement and transmission factors ranged from 0.88 to 0.93 for the 0 6 $\bar{1}\bar{2}$ and 0 2 1 reflections respectively.

7.3 SOLUTION AND REFINEMENT

For this crystal there were two possible space groups C_{2h}^{6} - C 2/c or C_{s}^{4} - C c and the molybdenum atoms had to occupy a 4-fold set of positions. For the space group C 2/c such positions have symmetry $\bar{1}$ or 2. As the compound contained a molybdenum(VI) dioxo group and since all such groups have been shown to adopt a cis configuration the choice of the two-fold axis must be the correct one if the latter space group is indicated. For the space group C c no symmetry requirements would be imposed on the molecule. Although intensity statistics were ambiguous (see table 7.1) it was felt that the centro-symmetric space group was the more likely choice and accordingly a Patterson function[258] was calculated. There proved to be some difficulty in solving this structure as the molybdenum was found to be on the two-fold axis with a Y coordinate very close to zero (Y = 0.009) introducing pseudosymmetry problems.

The first approach was made via solution of the Patterson function. If the molybdenum atom lay on a two-fold axis then

there should be Harker peaks found at 0, 2Y, ½. No such peaks were found although there were peaks present at 0, 0, ½. If the molybdenum atom was on a centre of symmetry then there would be peaks in the Patterson at 0, 0, ½. Alternatively, if the Y coordinate for a molybdenum atom on a two-fold axis was very close to zero then there would be a peak in the Patterson at 0, 0, ½. Since it seemed that a Y coordinate of zero was highly coincidental, and since further, the molecule could not possess a centre of symmetry, the alternative space group was chosen for subsequent calculations. After a number of unsuccessful attempts at solution in this space group (C c) attention was redirected to the centrosymmetric case.

An initial value for Y, the only unknown coordinate if the molybdenum atom is found on the two-fold axis, was chosen at 0.02. A structure factor calculation based on this trial solution gave values for R_1 and R_2 of 0.56 and 0.42 respectively. However, attempts to complete the structure using the normal difference Fourier methods gave trial structures which made little chemical sense and did not refine well. In all cases refinement converged to values of R_1 ca. 0.25.

Finally by calculating a map showing the observed electron density with signs based on a molbydenum position of Y = 0.017 and plotting the result on glass plates, positions for the chelate atoms about the molybdenum atom could be discerned. By choosing the eight chemically most reasonable peaks and placing these into a refinement cycle as carbon and oxygen atoms, values of R_1 and R_2 of 0.32 and 0.37 were obtained. After rejecting one peak which misbehaved and placing peaks found from a difference Fourier in a further refinement cycle, values of 0.21 and 0.22 were obtained for R_1 and R_2.

Further refinement followed by difference maps revealed the positions of all remaining nonhydrogen atoms and values of R_1 and R_2 converged at 0.15 and 0.10. An analysis of a calculated difference map showed peaks indicating considerable anisotropy in the thermal motions of all atoms. Allowance for this in a subsequent refinement cycle dropped the values of R_1 and R_2 to 0.13 and 0.09 respectively.

At this stage an analysis of the weighting scheme[273] showed that the stronger reflections were being underweighted and accordingly the data were reprocessed with a new p factor (see chapter 6 for discussion of weighting scheme) which increased the weight of these reflections. Absorption corrections were also applied to the data at this stage. Refinement of temperature and scale factors only lowered the values of R_1 and R_2 to 0.085 and 0.095 respectively. When all parameters were allowed to vary, refinement converged to values of $R_1 = 0.076$ and $R_2 = 0.068$. The shifts in all parameters were less than 1% of estimated standard deviations for these parameters.

Attempts to locate the hydrogen atoms either from the final difference map or via the calculated positions (by the program TETRIG)[267] were unsuccessful. A structure factor calculation using weak and unobserved reflections not used in the final refinement revealed no anomalies of the type $F_c >> F_o$. A final difference map was calculated and showed peaks of height up to 0.8 $\bar{e}/\text{Å}^3$ nearest the molybdenum atom. This was approximately one seventh the height of the last carbon atom included on the structure.

Positional and thermal parameters and their esd's[274] are listed in tables 7.2 and 7.3. Table 7.4 gives the root mean square amplitudes of vibration. Appendix H[277,278] contains a listing of the final values of F_0 and F_c for the 1123 reflections used in the refinement process.

7.4 DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Tables 7.5 and 7.6 give the intramolecular bond lengths and angles while table 7.7 gives the hydrogen bond lengths and angles. The crystal structure consists of molecules of $MoO_2(C_4H_9O_2)_2$ each surrounded by two molecules of $C_4H_{10}O_2$ which are attached by hydrogen bonds to the molybdenum complex and also linked by hydrogen bonds to neighbouring solvate molecules. Figure 7.1[275] shows the $MoO_2(C_4H_9O_2)_2$ unit while figure 7.2 shows how the molecules are packed in the unit cell. As can be seen from figure 7.2, the extensive hydrogen bonding has resulted in a layered structure.

All the atoms in the molecule exhibit considerable anisotropy in their thermal motion. An analysis of the root mean square amplitudes presented in table 7.4 shows that vibration in the z direction makes up the major component of this anisotropy.

Although the coordination number for the molybdenum atom is six there is considerable distortion from an ideal octahedral geometry due to the large O-Mo-O angle (105.2(5)°) for the dioxo group. This distorting effect of molybdenum terminal oxygen bonds is encountered in all molybdenum(V) and (VI) structures (see chapter 2). The angle subtended by the donor atoms of the chelating ligand has been compressed to 73.4(3)°.

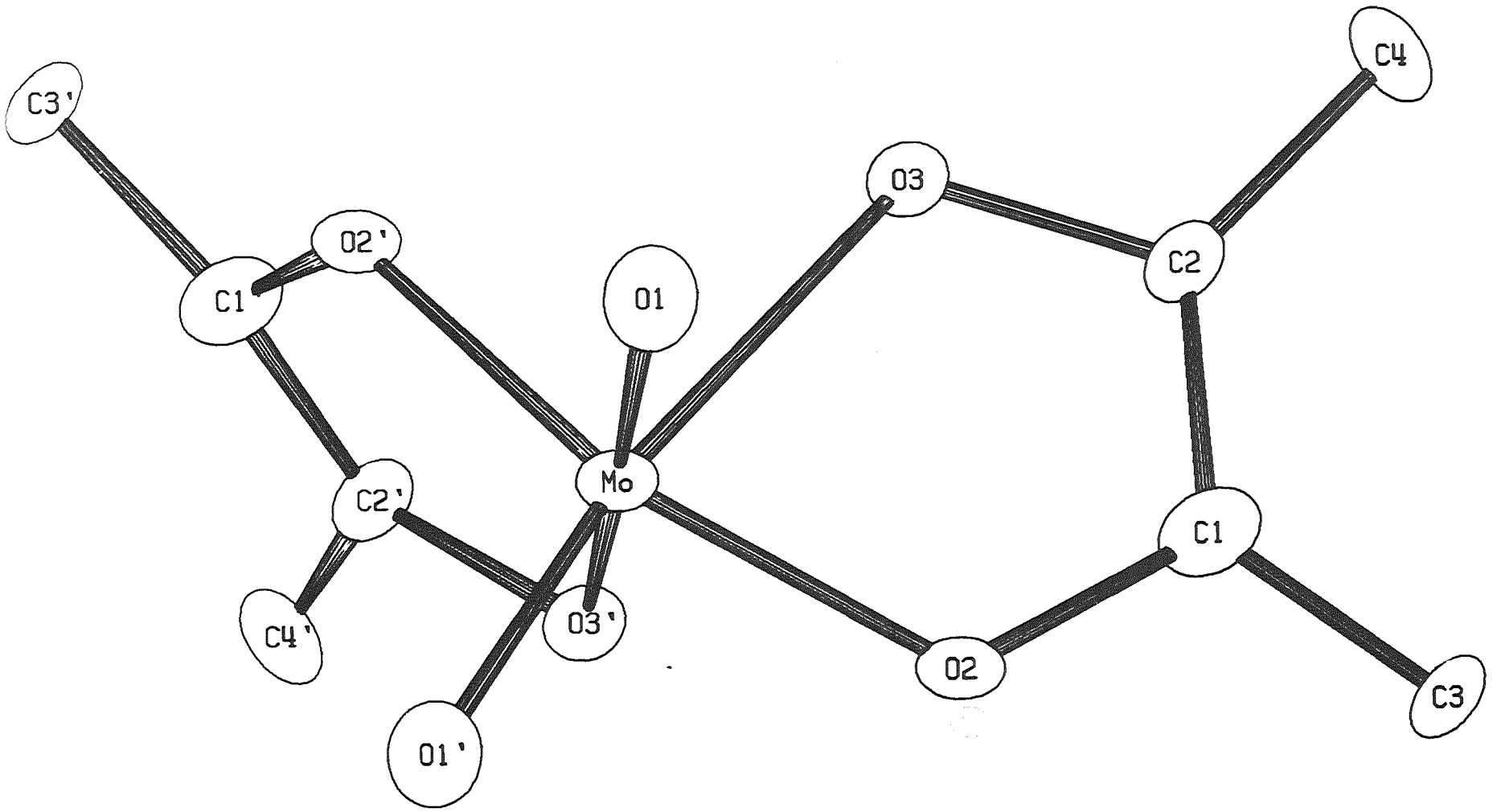


Figure 7.1(a) Structure of the $MoO_2(C_4H_9O_2)_2$ Unit

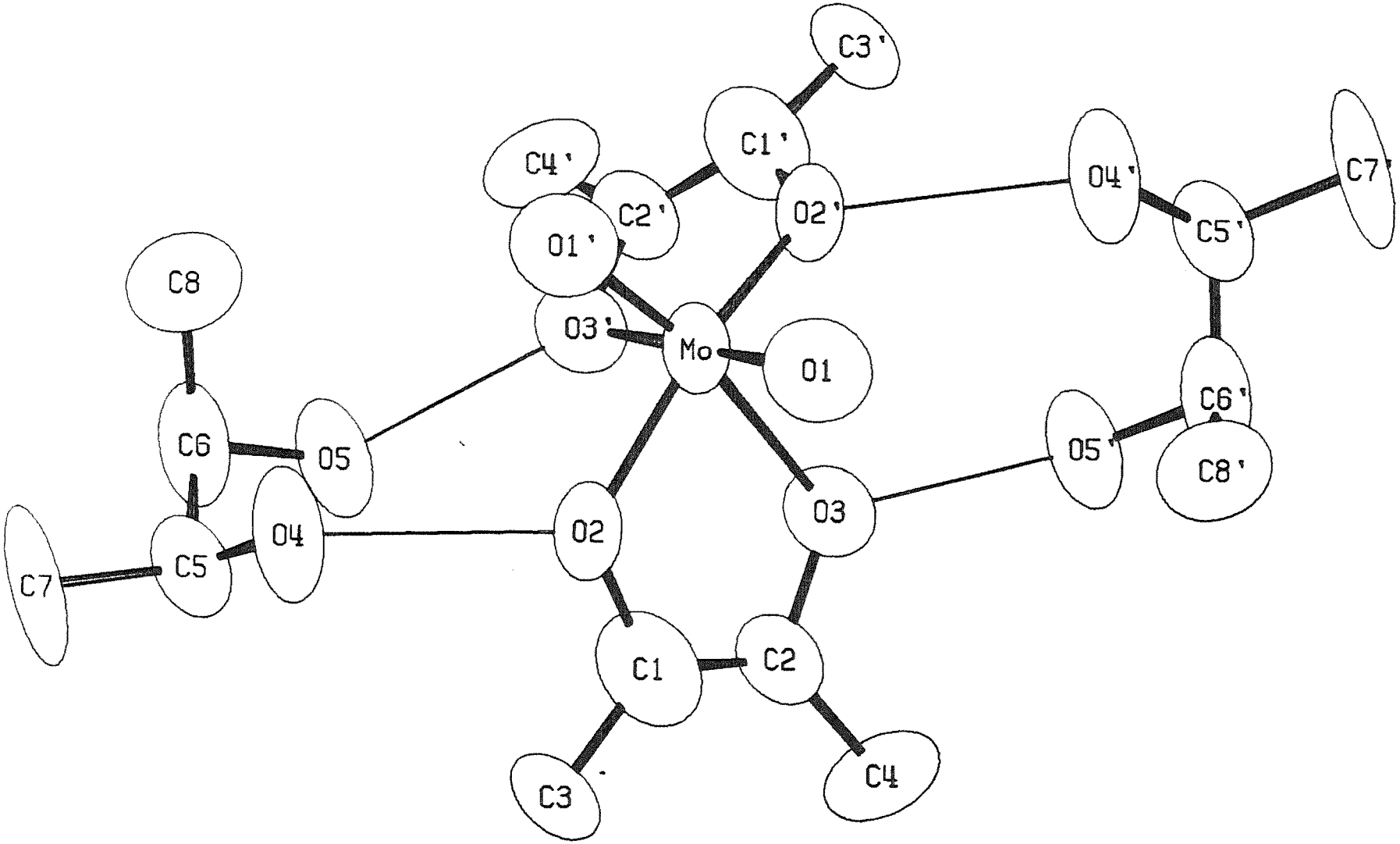


Figure 7.1(b) Structure of the $MoO_2(C_4H_9O_2)_2 \cdot 2C_4H_{10}O_2$ Unit

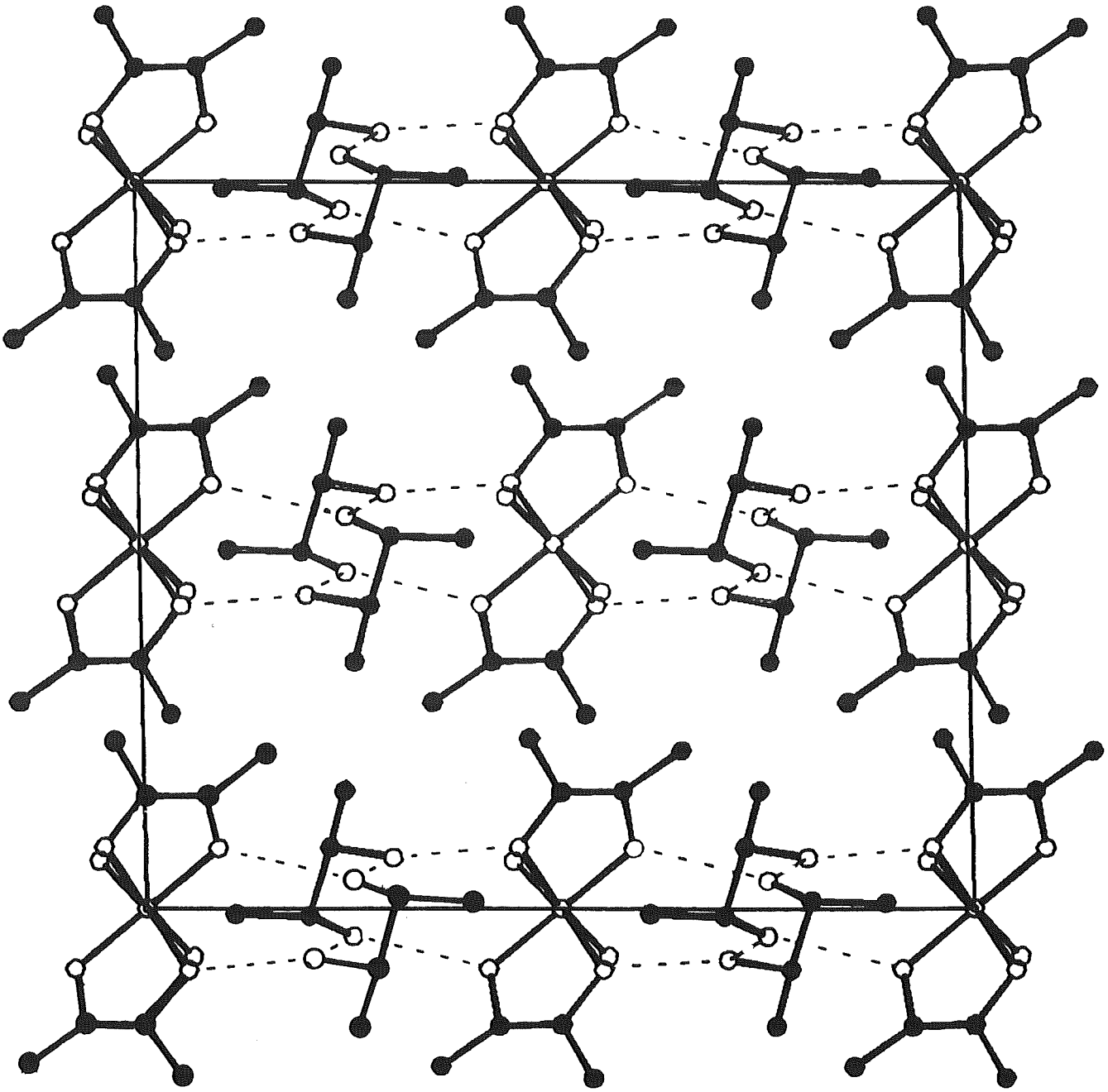


Fig. 7.2 Molecular Packing Diagram of the $MoO_2(C_4H_9O_2)_2 \cdot 2C_4H_1$ Units Viewed Down the b Axis.

Table 7.2

Positional Parameters for the Molybdenum Butanediol Complex

Atom	X	Y	Z
Mo	0.0	0.0090(1)	0.2500
O1	-0.0557(5)	-0.0936(8)	0.3156(6)
O2	0.0885(4)	0.0675(6)	0.3332(5)
O3	-0.0493(4)	0.1884(8)	0.3329(6)
O4	0.2513(4)	0.0259(7)	0.2883(6)
O5	0.2014(4)	0.2709(6)	0.1796(5)
C1	0.0752(8)	0.150(1)	0.414(1)
C2	0.0027(6)	0.234(1)	0.4069(8)
C3	0.1485(7)	0.188(1)	0.4671(9)
C4	-0.0340(8)	0.310(1)	0.482(1)
C5	0.3036(6)	0.138(1)	0.2627(9)
C6	0.2756(6)	0.194(1)	0.1667(9)
C7	0.3927(6)	0.081(1)	0.258(1)
C8	0.2578(8)	0.082(1)	0.089(1)

Table 7.3

Thermal Parameters for the Molybdenum Butanediol Complex

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.00324(6)	0.0086(2)	0.00747(9)	0.0	0.00081(5)	0.0
O1	0.0080(5)	0.020(1)	0.0089(6)	-0.0049(6)	0.0010(4)	0.0008(7)
O2	0.0032(3)	0.0123(8)	0.0079(5)	0.0006(4)	0.0010(3)	0.0014(6)
O3	0.0044(4)	0.021(1)	0.0108(6)	0.0041(5)	-0.0013(4)	-0.0075(8)
O4	0.0037(3)	0.013(1)	0.0144(7)	0.0022(5)	0.0020(4)	0.0042(7)
O5	0.0027(3)	0.0113(8)	0.0120(6)	0.0003(4)	0.0002(4)	-0.0006(6)
C1	0.0057(7)	0.024(2)	0.014(1)	0.004(1)	-0.0030(8)	-0.007(2)
C2	0.0038(5)	0.022(2)	0.0076(9)	0.0014(9)	-0.0013(6)	-0.002(1)
C3	0.0042(6)	0.040(3)	0.0089(9)	0.000(11)	-0.0023(6)	-0.005(2)
C4	0.0095(9)	0.033(3)	0.010(1)	0.007(1)	-0.0010(8)	-0.011(2)
C5	0.0026(5)	0.014(2)	0.012(1)	0.0005(8)	-0.0004(6)	0.001(1)
C6	0.0040(6)	0.014(2)	0.011(1)	0.0015(8)	0.0002(6)	0.002(1)
C7	0.0022(5)	0.019(2)	0.023(2)	0.0005(8)	0.0011(7)	0.002(1)
C8	0.0089(8)	0.018(2)	0.011(1)	0.000(1)	0.0007(8)	-0.004(1)

Table 7.4

Root Mean Square Amplitudes of Vibration for the Molybdenum Butanediol Complex

Atom	Displacement along X (Å)	Displacement along Y (Å)	Displacement along Z (Å)
Mo	0.203(2)	0.206(2)	0.281(2)
O1	0.24(1)	0.31(1)	0.38(1)
O2	0.200(9)	0.238(8)	0.297(9)
O3	0.19(1)	0.25(1)	0.41(1)
O4	0.20(1)	0.25(1)	0.41(1)
O5	0.19(1)	0.236(9)	0.354(9)
C1	0.24(2)	0.28(2)	0.45(2)
C2	0.20(2)	0.28(2)	0.34(1)
C3	0.20(2)	0.31(2)	0.45(2)
C4	0.21(2)	0.33(2)	0.49(2)
C5	0.18(2)	0.26(1)	0.36(2)
C6	0.21(2)	0.27(1)	0.34(2)
C7	0.17(2)	0.30(1)	0.49(2)
C8	0.26(2)	0.34(2)	0.37(2)

Table 7.5

Bond Lengths for the Molybdenum Butanediol Complex

Atom 1	Atom 2	Length Å
Mo	O1	1.662(7)
Mo	O2	1.935(7)
Mo	O3	2.284(7)
O2	C1	1.44(1)
O3	C2	1.41(1)
C1	C2	1.44(1)
C1	C3	1.44(2)
C2	C4	1.46(1)
O4	C5	1.44(1)
O5	C6	1.44(1)
C5	C6	1.54(2)
C5	C7	1.55(1)
C6	C8	1.59(2)

Table 7.6

Bond Angles for the Molybdenum Butanediol Complex

Atom 1	Atom 2	Atom 3	Angle(°)
O1	Mo	O1'	105.2(5)
O1	Mo	O2	103.9(3)
O1	Mo	O3	96.9(3)
O2	Mo	O2'	145.4(4)
O2	Mo	O3	73.4(3)
O3	Mo	O3'	78.6(4)
Mo	O2	C1	122.8(6)
Mo	O3	C2	115.0(6)
O2	C1	C2	114(1)
O2	C1	C3	115(1)
O3	C2	C1	110(1)
O3	C2	C4	118.1(9)
C1	C2	C4	126(1)
C2	C1	C3	124(1)
O4	C5	C6	109.6(9)
O4	C5	C7	107.1(8)
O5	C6	C5	107.9(9)
O5	C6	C8	108.3(9)
C5	C6	C8	114.8(9)
C6	C5	C7	110(1)

Table 7.7

Hydrogen Bond Lengths and Angles in the Molybdenum Butanediol Complex

Atom 1	Atom 2	Length	Atom 1	Atom 2	Atom 3	Angle
Intramolecular						
O4-H	O2	2.770(8)	C1	O2	O4	127.4(5)
O4'-H.....	O2'	2.770(8)	C5	O4	O2	121.3(5)
O3-H	O5'	2.606(9)	C2	O3	O5	122.3(5)
O3'-H.....	O5	2.606(9)	C6	O5	O3	128.6(6)
Intermolecular						
O5-H	O4	2.664(9)	C5	O4	O5	126.3(5)
O5'-H.....	O4	2.664(9)	C6	O5	O4	106.2(5)

A comparison of the lengths and angles of the cis-dioxo group in this structure with those found in other structures (table 7.8) shows that these values fall within the range expected, i.e. Mo = O from 1.63 to 1.83Å, and O = Mo = O from 102.2 to 106°, (the values for $[MoO_2F_4]^{42}$ (1.70(2)Å, 95(1)°) are anomalous and can perhaps be explained by the presence of the very electronegative fluorine atoms and their consequent withdrawal of electrons from the MoO_2^{2+} moiety).

An interesting feature of this structure is the presence of both "free" and coordinated ligand molecules giving an internal comparison on intra-ligand bond lengths and angles in both the free and complexed states. From chemical evidence (analyses and infrared spectra - see chapter 4) it is known that the ligand molecule loses a proton on coordination. Thus it would be expected that there would be two quite distinct Mo-O (ligand) bond lengths corresponding to the protonated and deprotonated donor oxygen atoms. However, the fact that one Mo-O (ligand) bond is trans to a terminal oxygen atom means that the Mo-O (ligand) bond will be longer than an exactly equivalent bond which was not trans to a terminal oxygen atom. Thus it is impossible to distinguish between the ligand oxygen atoms solely on the grounds of their bond lengths to molybdenum. However, it is of interest to examine the difference between the lengths and angles about the two oxygen atoms (see tables 7.5 and 7.6).

The two Mo-O lengths are 1.935(7) and 2.284(7)Å of which the former must correspond to the deprotonated -OH group. Table 7.9 shows a comparison of the distances and angles found in the free and complexed ligands. The difference in the two oxygen donors can be seen from the difference in both

Table 7.8

Bond Lengths and Angles for Molybdenum(VI) Dioxo Groupings

Structure	Mo-O1 (Å)	Mo-O2 (Å)	O1-Mo-O2 (°)	Reference No.
MoO_2(diethyldithiocarbamato)$_2$	1.63(2)	1.63(2)	103°†	189
$MoO_2Cl_2$2DMSO	1.64(1)	1.65(2)	102.4(8)	190
MoO_2Br_2Bipy	1.64(2)	1.83(2)	103.3(9)	4
$MoO_2Cl_2$2DMF	1.68(1)	1.68(1)	102.2(7)	41
$[MoO_2F_4]^-$	1.68(2)	1.73(1)	95(1)	42
$[MoO_2(C_2O_4)H_2O]_2O$	1.68(2)	1.70(2)	106(1)	5
$MoO_2$2acac	1.69(*)	1.69(*)	105(*)	44
$MoO_2$2oxine	1.71(2)	1.71(2)	104.1(7)	43
MoO_2 atran	1.75(4)	1.80(4)		26
	(1.77(4))	1.83(4)		

* Not reported in this paper.

† Calculated from the atomic coordinates quoted.

DMSO = dimethylsulphoxide

Bipy = α,α'-bipyridyl

DMF = dimethylformamide

acac = pentane-3,4-dionato

oxine = 8-quinolinolato

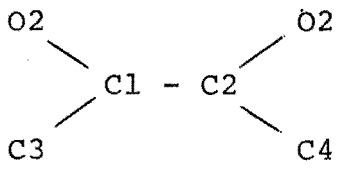
atran = nitrilotri(2-hydroxyethane)

Table 7.9

Bond Lengths and Angles for Free and Complexed Butanediol

Bond Length*	Value in Free Butanediol	Value in Complexed Butanediol
C1-O1	1.44(1)Å	1.44(1)Å
C2-O2	1.44(1)Å	1.41(1)Å
C1-C2	1.54(1)Å	1.44(1)Å
C1-C3	1.55(1)Å	1.44(2)Å
C2-C4	1.59(2)Å	1.46(1)Å
Bond Angle*		
O1-C1-C2	109.6(9)°	114(1)°
O2-C2-C1	107.9(9)°	110(1)°
O1-C1-C3	107.1(8)°	115(1)°
O2-C2-C4	108.3(9)°	118.1(9)°
C3-C1-C2	110(1)°	124(1)°
C4-C2-C1	114.8(9)°	126(1)°

* Numbering sequence related to diagram below for both molecules for this table only, to facilitate comparison.



the carbon oxygen bond lengths and in the molybdenum oxygen carbon bond angles. The deprotonated oxygen donor has a shorter bond to the molybdenum atom and a longer bond to the carbon atom while the angle subtended about this oxygen atom by the molybdenum and carbon atoms is greater than that found for the other donor oxygen group (-OH).

The distortions imposed on the ligand by chelation can be readily seen from the fact that in the free ligand the distance between oxygen atoms is 2.97(1)Å while in the complexed ligand this distance is reduced to 2.53(1)Å. On the other hand chelation has increased the distance between the two methyl groups and consequently the C(3)-C(1)-C(2) and C(4)-C(2)-C(1) angles are increased from 110(1) and 114.8(9)° in the free ligand to 124(1) and 126(1)° in the complexed ligand.

The carbon carbon bond length in the chelate ring (C(1)-C(2) is significantly shorter at 1.44(1)Å than that found in the free ligand (C(5)-C(6)) at 1.54(1)Å. Also the angles subtended at C(1) and C(2) in the chelate ring and C(5) and C(6) in the free ligand molecule show considerable differences. In the latter case they are all near the expected tetrahedral value of 109.8° while in the former case they are all intermediate between the tetrahedral and trigonal (120°) values. A further point is the fact that the chelate rings are almost planar (see table 7.10 for the results of mean plane[276] calculations). The angles subtended at the carbon atoms show this change quite clearly. For C(5) and C(6) the sums of the subtended angles are 326.7° and 331.0° respectively while at C(1) and C(2) these sums are 353 and 354° respectively. An explanation for these results could be in terms of some degree of electron delocalization about the chelate ring making the two oxygen atoms almost equivalent.

Table 7.10

Results of Several Mean Plane Calculations for Selected Planes

Plane 1	(Å)	(Å)
Atoms in Plane	Deviation From Plane(P)	Esd(P)
Mo	-0.002	0.001
O2	0.083	0.007
O3	0.154	0.008
C1	-0.14	0.015
C2	0.02	0.013
C3	-0.02	0.015
C4	0.32	0.016
Equation of Least Squares Mean Plane		
0.3262X + 0.6906Y - 0.6455Z + 2.2711 = 0		
Plane 2	(Å)	(Å)
Atoms in Plane	Deviation from Plane(P)	Esd(P)
Mo	0.002	0.001
O2'	-0.083	0.007
O3'	-0.154	0.008
C1'	0.14	0.015
C2'	-0.02	0.013
C3'	0.02	0.015
C4'	-0.32	0.016
Equation of Least Squares Mean Plane		
0.3262X - 0.6906Y - 0.6455Z + 2.3586 = 0		
Angle Between Planes 1 and 2 is 94.4°		

In this structure there is a comprehensive hydrogen bonding system attaching the solvate molecules to the complex and extending in layers throughout the structure (see figure 7.2). The criterion for a hydrogen bond involving oxygen atoms appears to be a contact distance less than 2.8Å since the Van der Waals radius of an oxygen atom is 1.4Å [268], corresponding to a closest approach of two non-bonded oxygen atoms of 2.8Å. It is also necessary for a hydrogen atom to be attached to one of the oxygen atoms and directed along a line joining their centres (deviations from this line of up to 15° have been found in other cases[269]).

Each central entity of $MoO_2(C_4H_9O_2)_2$ has two molecules of butane-2,3-diol attached to it in such a way that the two ligand molecules are linked by two hydrogen bonds to one solvate molecule (see figure 7.1(b)). Also there is hydrogen bonding between solvate molecules so that each grouping of $MoO_2(C_4H_9O_2)_2.2(C_4H_{10}O_2)$ is linked to a neighbouring molecular grouping making a layered structure.

Although the structure of $MoO_2(C_4H_9O_2)_2.2(C_4H_{10}O_2)$ as determined by an X-ray structure analysis is not the same as that proposed on the basis of chemical and physical studies it is of interest to see how the determined structure accounts for the structural evidence obtained from these studies. The infrared spectrum was consistent with four equivalent monodentate butane-2,3-diol molecules. In view of the considerable modification undergone by the ligand molecule on coordination this result is surprising, however, it should be noted that comparison of the infrared spectrum of the ethane-1,2-diol with that of its molybdenum complex shows that while band shape

Table 7.11

Selected Inter- and Intramolecular Nonbonding Contact Distances (< 3.5Å)

Atom 1	Atom 2	Distance Å
Intramolecular Contacts		
Mo	C1	2.961
O1	O1'	2.640
O2	C2	2.417
O2	O3	2.533
O3	C1	2.341
O4	C7	2.426
O4	O5	2.987
O5	C5	2.425
C3	O2	2.449
C4	O3	2.471
C6	O4	2.451
C8	O5	2.489
Intermolecular Contacts		
O1	C7	3.421
O2	O1'	2.830
O4	C6'	3.369
C1	O1'	3.497
C6	O4'	3.369

and position are changed there is considerable sharpening of these bands in the chelate compared with the broad bands found in the ligand. The butane-2,3-diol compound has both 'free' and complexed ligand molecules and the sharp bands of the latter could be hidden under the broad bands of the former. A close reexamination of the spectrum of the complex shows that small shoulders do appear on some bands (see figure 3.5).

Conductometric measurements and NMR spectra indicated that some of the ligand molecules were labile in solution. This fact is readily accounted for by the two solvate molecules. The strength of the attachment of the solvate molecules to the central entity is illustrated by the fact that only after 24 hours pumping under a hard vacuum at temperatures greater than 100^{o}C could these solvate molecules be removed[270].

Finally, the most surprising result of all is the fact that in a mass spectrum of the compound a molecular ion peak centred about 486 m/$\bar{e}$ (there are seven isotopes of molybdenum with relative abundances greater than 10%) was detected indicating either that the hydrogen bonds persist in the gaseous phase or that the compound rearranges in the vapour phase to one with four monodentate ligands. Both of these explanations appear unlikely although evidence gained from recrystallisations from dilute solutions and also from attempts to remove the solvate butane-2,3-diol molecules shows that the hydrogen bonds between the solvate molecules and the central entity are strong.

CHAPTER 8

THE CRYSTAL AND MOLECULAR STRUCTURE OF $NH_4[MoO_2(C_8H_7O_7N_3)]H_2O$

8.1 INTRODUCTION

In the course of the experimental work associated with this project a molybdenum(V) complex of urmail-N,N-diacetic acid was prepared. From the evidence gathered during the characterisation of this compound it was believed that it contained a molybdenum(V) dioxo group. In view of the current interest in the stereochemistry of metal oxo cations[37,47,279] it was decided that a full X-ray structure analysis was warranted. A structural characterisation of a molybdenum(V) dioxo group is of significance in view of the fact that although the stereochemistry of both d^0 and d^2 dioxo groups has been well established as *cis*[41] and *trans*[280] respectively, for a d^1 configuration two possibilities may arise. Either a *cis* or a *trans* arrangement may occur depending on whether the unpaired d electron occupies an antibonding orbital or a non-bonding orbital localized on the metal atom. Atovmyan and Porai-Koshits[37] expected a *cis* configuration for a molybdenum(V) mononuclear dioxo grouping but remarked on the absence of examples of compounds containing this group. Thus the characterisation of the stereochemistry of this group is of importance in the general context of the structural chemistry of metal oxo cations.

8.2 EXPERIMENTAL

The complex $NH_4[MoO_2(C_8H_7O_7N_3)]H_2O$ was prepared by mixing aqueous solutions of $(NH_4)_2MoOCl_5$ and uramil-N,N-diacetic acid and adjusting the pH to a value of 3.5 with dilute ammonia. Yellow crystals in the form of truncated rectangular prisms were obtained by slow evaporation of this solution.

Crystallographic Data

$MoC_8H_{13}O_{10}N_4$, F.W. = 421.1, is monoclinic with $\underline{a}$ = 6.744(1), $\underline{b}$ = 18.071(4), $\underline{c}$ = 11.500(3)Å, β = 102.01(5)°; $\underline{U}$ = 1400.7Å^3; $\underline{D}_m$ = 2.01(1)g.cm^{-3}, $\underline{D}_c$ = 1.976 g.cm^{-3}, z = 4 F(000) = 844, μ(MoKα) = 9.91 cm^{-1}.

Systematic absences occurred for $\underline{h}$ o $\underline{\ell}$ reflections when $\underline{\ell}$ was odd and for o $\underline{k}$ o reflections when $\underline{k}$ was odd uniquely determining the space group as $\underline{P}\ 2_1/\underline{c}$. Unit cell dimensions and their esd's were obtained by least squares refinement of the setting angles of twelve reflections accurately centred on a 3.5 mm diameter circular receiving aperture in the manner given by Busing[266] and outlined more fully in chapter 6. The experimental density was determined by a pycnometric method using iodomethane and tetrachloro methane for flotation.

Diffraction data were obtained from a crystal whose shape approximated that of a truncated rectangular prism with boundary faces defined by the forms {100}, {$\bar{1}$00}, {0$\bar{1}$0}, {00$\bar{1}$}, {011} and {0$\bar{1}\bar{1}$}. Crystal dimensions normal to these forms and taken from an arbitrary origin at the centre of the crystal were 0.19, 0.19, 0.21, 0.21, 0.08 and 0.08 mm respectively. A preliminary mosaicity check of the crystal showed that the width at half height of intense low angle reflections was

acceptably low at 0.15°. Intensity data were recorded as described in chapters 6 and 7. A total number of 2664 reflections were collected in this way, and, after averaging of equivalent forms, there was a total of 1901 independent reflections recorded within the range $0 < 2\theta \leqslant 46^{\circ}$ of which 1601 were greater than $3\sigma(I)$ and 159 were considered as unobserved as they had intensities less than $\sigma(I)$.

Absorption corrections were applied before the final refinement and the transmission factors ranged from 0.67 to 0.88 for the 011 and $02\bar{1}$ reflections respectively.

8.3 SOLUTION AND REFINEMENT

The position of the molybdenum atom was determined from a consideration of the Harker peaks of a Patterson map. A structure factor calculation based on this atom alone gave values for R_1 and R_2 of 0.47 and 0.56 respectively. A difference map revealed the presence of two peaks in the vicinity of molybdenum in chemically reasonable positions. Inclusion of these in a structure factor calculation lowered the values of R_1 and R_2 to 0.38 and 0.47 respectively. Subsequent difference maps followed by structure factor calculation revealed the positions of the remaining atoms in the ligand molecule. Refinement of the positional and thermal parameters for these atoms lowered the values of R_1 and R_2 to values of 0.12 and 0.18 respectively. A difference map calculated on the basis of this model revealed the presence of two further peaks. Chemical analysis had indicated a formula of $NH_4[MoO_2UDA].H_2O$ and although on the basis of crystallographic evidence it cannot be assumed that the two extra atoms are

from NH_4^+ and H_2O it is chemically reasonable to assume this. Accordingly two oxygen atoms were included in subsequent calculations at the indicated positions. The presence of large peaks close to the molybdenum atom indicated that this atom was vibrating anisotropically. Subsequent refinement with the molybdenum atom allowed to vibrate anisotropically and including the new atoms gave values of $R_1 = 0.052$ and $R_2 = 0.078$. The two new atoms had widely different temperature factors (5.2 and 7.2) and in subsequent calculations the latter was treated as a nitrogen atom, assumed to be an ammonium ion. Following refinement the new temperature factors were 5.2 and 5.4 respectively, while R_1 and R_2 had values of 0.053 and 0.080 respectively.

At this point analysis of the weighting scheme showed that the stronger reflections were being underweighted and accordingly the data were reprocessed with a new p factor (see chapter 6 for the significance of this change) which increased the weight of these reflections. Absorption corrections were also applied at this stage and refinement allowing only temperature and scale factors to vary lowered R_1 and R_2 to 0.051 and 0.070 respectively. Refinement allowing all parameters to vary lowered R_1 and R_2 to 0.050 and 0.068.

Positions for the hydrogen atoms were then calculated on the basis of tetrahedral or trigonal geometry with a calculated carbon hydrogen bond length of 1.073Å and a calculated nitrogen hydrogen bond length of 1.038Å (using program TETRIG[267]). These calculated positions were verified by an examination of the difference Fourier map and in all cases corresponded to regions of significant electron density. Hydrogen atoms were placed in their calculated positions with a temperature factor of 5.0. Further refinement, while not varying the parameters

for the hydrogen atoms, lowered the values for R_1 and R_2 to 0.048 and 0.064 respectively.

A structure factor calculation using the weak and unobserved reflections not used in the final refinement showed no anomalies of the type $F_c >> F_0$. Shifts in the parameters in the final refinement were less than 1 percent of their esd's and all correlation coefficients were less than 0.6. Accordingly the refinement was assumed to have converged. Calculation of a final difference map showed peaks of a maximum height of 1.4 $\bar{e}/\text{Å}^3$ while the height of the last non-hydrogen peak included in the calculations was 6.6 $\bar{e}/\text{Å}^3$.

Positional and thermal parameters and their esd's are shown in table 8.1 while table 8.2 gives the root mean square amplitudes of vibration of the molybdenum atom. Appendix I contains a listing of the 1748 reflections used in the final refinement process.

8.4 DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure consists of an assemblage of NH_4^+ cations, $[MoO_2(C_8H_7N_3O_7)]^-$ anions and water molecules which are interconnected by hydrogen bonds. The anion is illustrated in figure 8.1 which also gives the atom numbering scheme. Table 8.3 gives a listing of the bond lengths while table 8.4 gives a listing of the bond angles for the anion. The anions are well separated in space with the nearest nonbonding contact being 2.905(8) Å involving the atoms O(6) and N(4) (this is potentially a hydrogen bond contact although the angles about the N(4) atom tend to exclude this possibility). Other non-bonding contacts are presented in table 8.6.

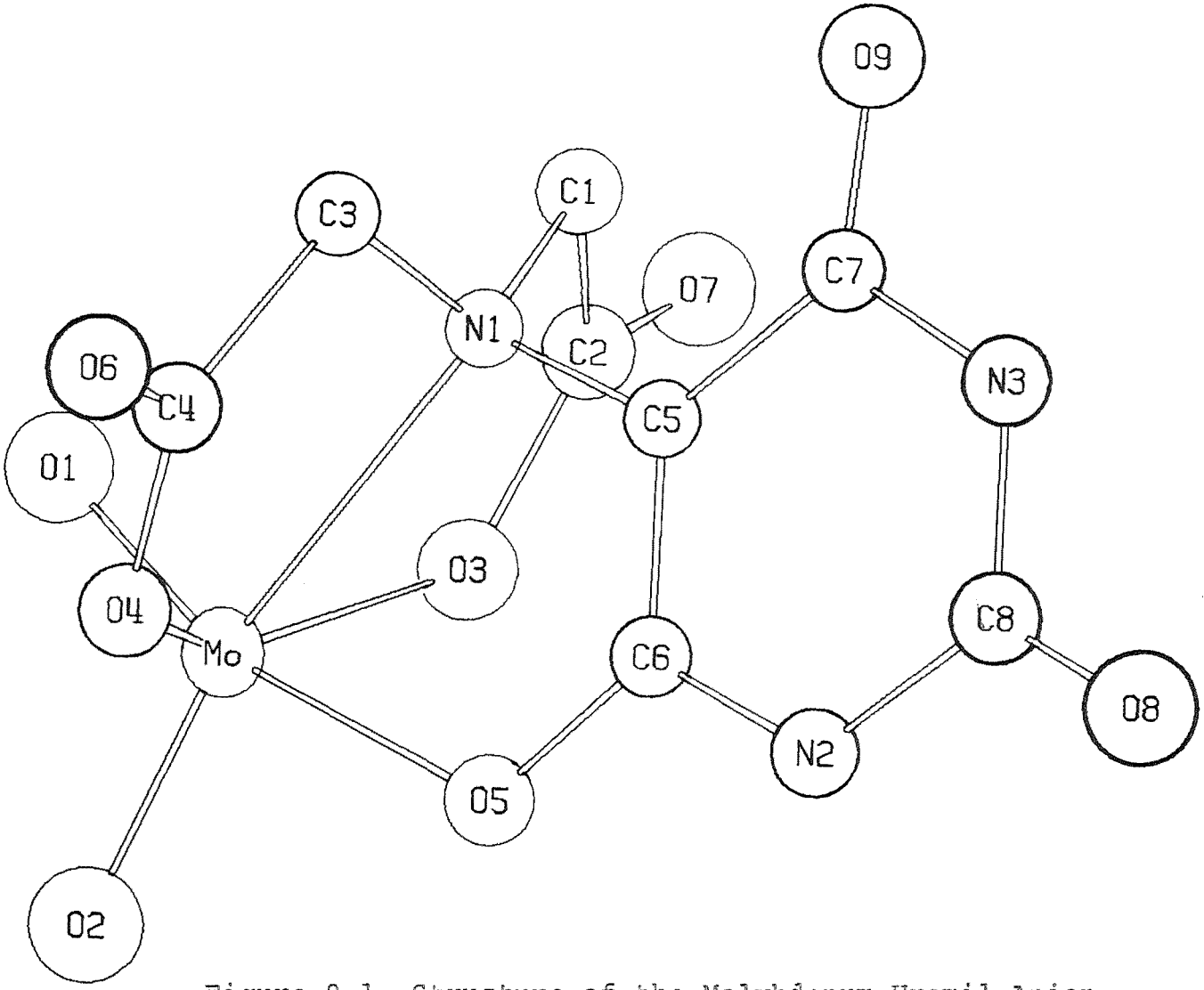


Figure 8.1 Structure of the Molybdenum Uramil Anion

Table 8.1

Positional and Thermal Parameters for the Molybdenum Uramil Structure

Atom	X	Y	Z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.12042(8)	-0.21973(3)	0.23289(5)	0.0125(2)	0.00169(2)	0.00367(6)	-0.00046(4)	-0.00004(7)	-0.00045(3)
O1	0.2747(8)	-0.2553(3)	0.1486(4)	3.4(1)					
O2	-0.1181(8)	-0.2380(3)	0.1613(5)	3.8(1)					
O3	0.1884(7)	-0.2978(3)	0.3569(4)	2.88(9)					
O4	0.1648(6)	-0.1144(2)	0.1840(4)	2.40(8)					
O5	0.00198(6)	-0.1649(2)	0.3688(4)	2.32(8)					
O6	0.38211(7)	-0.0250(2)	0.1715(4)	2.84(9)					
O7	0.42697(8)	-0.3642(3)	0.4748(4)	3.6(1)					
O8	0.1032(7)	-0.0260(3)	0.7048(4)	3.5(1)					
O9	0.6580(7)	-0.0980(3)	0.5673(4)	3.0(1)					
O10	0.2300(9)	0.0386(4)	0.9354(5)	5.6(1)					
N1	0.4067(7)	-0.1771(3)	0.3671(4)	1.72(9)					
N2	0.0535(8)	-0.0955(3)	0.5362(4)	2.1(1)					
N3	0.3806(8)	-0.0632(3)	0.6352(4)	2.1(1)					
N4	0.121(1)	0.1040(4)	1.1241(7)	5.4(2)					

(contd)

Table 8.1

Atom	X	Y	Z	B or 11	22	33	12	13	23
C1	0.521(1)	-0.2445(4)	0.4152(6)	2.2(1)					
C2	0.376(1)	-0.3068(4)	0.4185(6)	2.5(1)					
C3	0.5082(9)	-0.1292(3)	0.2933(5)	1.97(1)					
C4	0.343(1)	-0.0846(4)	0.2114(6)	2.1(1)					
C5	0.3360(9)	-0.1345(3)	0.4581(5)	1.6(1)					
C6	0.1309(9)	-0.1333(3)	0.4521(5)	1.8(1)					
C7	0.4700(9)	-0.0990(3)	0.5518(5)	1.8(1)					
C8	0.176(1)	-0.0606(4)	0.6297(6)	2.3(1)					
H1*	0.6253	-0.2588	0.3597	5.0					
H2	0.6053	-0.2328	0.5036	5.0					
H3	0.6127	-0.0920	0.3490	5.0					
H4	0.5916	-0.1620	0.2417	5.0					
H5	-0.0292	-0.1347	0.5736	5.0					
H6	0.4424	-0.0889	0.7167	5.0					

* H positions calculated by TETRIG.

Table 8.2

Root Mean Square Amplitudes of Vibration for Molybdenum

Atom	Displacement along X Å	Displacement along Y Å	Displacement along Z Å
Molybdenum	0.135(1)	0.174(1)	0.181(1)

Table 8.3

Bond Lengths for the Molybdenum Uramil Complex

Atom 1	Atom 2	Length (Å)	Atom 1	Atom 2	Length (Å)
Mo	O1	1.689(5)	C3	N1	1.477(8)
Mo	O2	1.680(5)	C5	N1	1.457(7)
Mo	O3	1.991(5)	C6	N2	1.372(8)
Mo	O4	2.024(4)	C8	N2	1.366(8)
Mo	O5	2.140(4)	C7	N3	1.394(8)
Mo	N1	2.337(5)	C8	N3	1.370(8)
C2	O3	1.325(8)	C1	C2	1.498(9)
C2	O7	1.232(8)	C3	C4	1.530(9)
C4	O4	1.294(7)	C5	C6	1.371(8)
C4	O6	1.221(7)	C5	C7	1.409(8)
C6	O5	1.286(7)			
C7	O9	1.244(7)			
C8	O8	1.246(7)			
C1	N1	1.486(8)			

Table 8.4

Bond Angles for the Molybdenum Uramil Complex

Atom 1	Atom 2	Atom 3	Angle(°)	Atom 1	Atom 2	Atom 3	Angle(°)
O1	Mo	O2	106.6(2)	O3	C2	O7	121.0(6)
O1	Mo	O3	93.6(2)	O4	C4	O6	122.6(6)
O1	Mo	O4	93.1(2)	C1	C2	O3	116.8(6)
O1	Mo	O5	164.3(2)	C1	C2	O7	122.2(6)
O1	Mo	N1	88.9(2)	C3	C4	O4	116.8(6)
O2	Mo	O3	105.4(2)	C3	C4	O6	120.6(6)
O2	Mo	O4	103.3(2)	C2	C1	N1	109.5(5)
O2	Mo	O5	89.1(2)	C4	C3	N1	107.2(5)
O2	Mo	N1	164.4(2)	C6	C5	N1	111.3(5)
O3	Mo	O4	147.1(2)	C7	C5	N1	116.8(5)
O3	Mo	O5	82.6(2)	C5	C6	N2	120.0(6)
O3	Mo	N1	74.1(2)	C5	C7	N3	115.9(5)
O4	Mo	O5	82.4(2)	C1	N1	C3	115.3(5)
O4	Mo	N1	74.0(2)	C1	N1	C5	112.8(4)
O5	Mo	N1	75.4(2)	C3	N1	C5	111.3(5)
Mo	O3	C2	121.4(4)	C6	N2	C8	121.9(5)
Mo	O4	C4	120.5(4)	C7	N3	C8	124.1(5)
Mo	O5	C6	116.9(4)	N2	C8	N3	117.2(6)
Mo	N1	C1	105.6(3)	N2	C8	O8	121.2(6)
Mo	N1	C3	103.4(3)	N3	C8	O8	121.5(6)
Mo	N1	C5	107.4(3)	N3	C7	O9	118.0(5)
C5	C6	O5	123.3(6)	N2	C6	O5	116.7(5)
C5	C7	O9	126.0(5)				

Table 8.5

Hydrogen Bond Lengths and Angles for the Molybdenum Uramil Structure

Intraanionic Bond Lengths			Interanionic Bond Lengths		
Atom 1	Atom 2	Length(Å)	Atom 1	Atom 2	Length(Å)
O10	N4	2.74(1)	O10	O6	2.897(8)
O10	O8	2.825(8)	N4	O3	2.781(9)

Hydrogen Bond Angles

Atom 1	Atom 2	Atom 3	Angle(°)
O6	O10	O8	136.0(3)
O3	N4	O10	133.4(3)

Table 8.6

Selected Non Bonding Contact Distances for the Molybdenum Uramil Complex

Intramolecular			Intermolecular		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Mo	C4	2.903(6)	O1	C6	3.032(8)
O1	O3	2.692(8)	O2	C1	3.341(8)
O1	O2	2.702(8)	O3	O1	3.421(8)
O2	O5	2.699(8)	O4	O10	3.096(9)
O3	O7	2.227(9)	O6	N4	2.905(8)
O4	O6	2.206(8)	O7	C4	3.037(8)
O5	N2	2.263(8)	O8	N4	3.063(8)
O7	C1	2.395(8)	O9	O2	3.399(8)
O8	N2	2.277(8)	O10	O7	2.972(8)
O9	N3	2.262(8)	N2	O1	3.220(8)
N1	C6	2.408(8)	N3	O6	2.926(8)
C1	O7	2.395(9)	C2	O1	3.080(8)
C2	N1	2.437(8)	C5	O1	3.052(8)
C3	O6	2.394(8)	C7	O1	3.244(8)
C4	N1	2.421(8)	C8	O1	3.392(8)
C5	O5	2.338(8)			
C6	C8	2.394(8)			
C7	C6	2.416(8)			

The structure is held together in a closely packed arrangement by a system of hydrogen bonds involving the water molecule and ammonium cation. Each of these two entities forms two hydrogen bonds, the hydrogen atoms of the water molecule linking neighbouring anions through atoms O(6) and O(8) while the ammonium cation forms hydrogen bonds with the water molecule and the O(3) atom of a neighbouring anion. Table 8.5 lists the hydrogen bond lengths and angles.

Although the long term significance of this structure lies in the presence of a monomeric cis-dioxo grouping for molybdenum(V), in terms of coherence in presentation the coordination environment about the molybdenum atom will be discussed first. This coordination environment is made up of two terminal oxygen atoms, two carboxylate oxygen atoms, a carbonyl oxygen atom, and a tertiary nitrogen atom. The uramil-N,N-diacetate molecule is behaving as a tetradentate ligand in this compound although its usual mode of coordination is in a tridentate fashion (see chapter 4). The fourth donor atom is the carbonyl oxygen of the pyrimidine ring, a significant point as earlier chemical studies carried out in this project (see chapter 4) have indicated that the pyrimidine ring as found in barbituric acid, alloxazine and riboflavin does not interact strongly with metals such as copper and molybdenum.

The stereochemistry of the dioxo grouping in this anion is cis and a comparison of the bond lengths and angles found in this with those found for structurally characterised molybdenum(VI) complexes with dioxo groups (see table 8.7) is of interest. The two molybdenum terminal oxygen bond lengths agree within statistical limits of error and their average

Table 8.7

Bond Lengths and Angle for Molybdenum(VI) Dioxo Groupings

Structure	Mo-O1 (Å)	Mo-O2 (Å)	O1-Mo-O2 (°)	Reference
MoO_2(diethyldithiocarbamate)$_2$	1.63(2)	1.63(2)	103†	189
MoO_2Cl_2.2DMSO	1.64(1)	1.65(2)	102.4(8)	190
MoO_2Br_2.Bipy	1.64(2)	1.83(2)	103.3(9)	4
MoO_2(butanediol)$_2$.2Butane-diol	1.662(7)	1.662(7)	105.2(5)	Chapter 8
MoO_2Cl_2.2DMF	1.68(1)	1.68(1)	102.2(7)	41
$[MoO_2F_4]^-$	1.68(2)	1.73(1)	95(1)	42
$[MoO_2(C_2O_4)H_2O]_2O$	1.68(2)	1.70(2)	106(1)	5
MoO_2acac_2	1.69(*)	1.69(*)	105(*)	44
MoO_2oxine_2	1.71(1)	1.71(1)	104.1(7)	43
MoO_2 atran	1.75(4)	1.80(4)	(*)	26
(2nd independent mol.)	(1.77(4))	1.83(4)		

* Not reported in this paper

† calculated from atomic coordinates given

DMSO = dimethylsulphoxide

Bipy = α,α'-bipyridyl

DMF = N,N-dimethylformamide

acac = pentane-2,4-dionato

oxine = 8-quinolinolato

atran = nitrilotri(2hydroxyethane)

value is 1.684(5) Å, which places it within the range expected for the molybdenum (VI) cases, whilst the O(1)-Mo-O(2) angle of 106.6(2)° is also comparable with that found in molybdenum (VI) structures.

Table 8.10 presents values for the bond angles and bond lengths found in the two glycinato rings in this structure. Comparison of the bond parameters of the chelate framework reveals only one significant difference, i.e. that the molybdenum oxygen length in ring II is 0.03Å longer than that found for the analogous bond in ring I. Inasmuch as the complexing bonds are where ring strain is concentrated[1], the greater length of the MoO(4) bond suggests greater strain in ring II, a conclusion that is confirmed by analysis of the bond angle data.

The carbon oxygen bond lengths for the complexed oxygen (O_c) and uncomplexed (O_u) oxygen atoms in the carboxylate groups in the two rings are 1.324(8) and 1.233(8)Å for ring I and 1.294(7) and 1.221(7)Å for ring II. These differences in bond length between the C-O_c and C-O_u bonds of 0.092Å and 0.073Å are almost twice those found in the corresponding molybdenum(VI) EDTA structure[1] and reflect the greater strength of the molybdenum(V) oxygen bond in this compound as also do the shorter molybdenum oxygen (and molybdenum nitrogen) bond lengths. An explanation for this somewhat unexpected result lies in the fact that the EDTA complex contains a cis-trioxo molybdenum(VI) grouping. The π-bonding in molybdenum(V) and (VI) compounds is concentrated in bonds to terminal oxygen atoms at the expense of those to other atoms in a mixed complex[21] and hence the bonding to these other atoms will be

Table 8.8

Results of Mean Plane Calculations for Selected Groups of Atoms

Plane 1

Atoms in Plane	Deviation from Plane (P) in Å	Esd(P) in Å
Mo	-0.0001	0.0006
O1	0.042	0.005
O2	0.064	0.005
O5	-0.053	0.004
O8	0.034	0.005
O9	0.016	0.005
N1	-0.058	0.005
N2	-0.006	0.005
N3	0.012	0.005
C5	-0.001	0.006
C6	-0.031	0.006
C7	0.019	0.006
C8	0.000	0.006

Equation of Least Squares Mean Plane for Plane 1

$$0.0620X + 0.8427Y - 0.5349Z + 4.7311 = 0$$

Plane 2

Atoms in Plane	Deviation from Plane (P) in Å	Esd(P) in Å
O8	0.008	0.005
O9	0.000	0.005
N2	0.000	0.005
N3	-0.008	0.005
C7	0.011	0.006
C8	-0.014	0.006
Atom	**Distance from Plane**	**Esd in Å**
Mo	0.0583	0.0006
O1	0.111	0.005
O2	0.141	0.005
O5	-0.015	0.004
N1	-0.031	0.005
C5	0.011	0.006
C6	-0.011	0.006

Equation of Least Squares Mean Plane for Plane 2

$$0.0574X + 0.8353Y - 0.5469Z + 4.7927 = 0.$$

Table 8.8 (contd)

Plane 3

Atoms in Plane (P)	Deviation from Plane (P) Å	Esd(P) Å
Mo	0.0025	0.0006
O3	-0.209	0.005
C2	0.140	0.007
C1	0.344	0.006
N1	-0.235	0.005

Equation of the Least Squares Mean Plane for Plane 3

$$0.6495X - 0.4901Y - 0.6409Z - 0.1086 = 0$$

Plane 4

Atoms in Plane (P)	Deviation from Plane (P) Å	Esd(P) Å
Mo	0.0028	0.0006
O4	-0.187	0.004
C4	0.096	0.006
C5	0.416	0.006
N1	-0.297	0.005

Equation of the Least Squares Mean Plane for Plane 4

$$0.6284X - 0.4256Y - 0.6511Z - 0.1414 = 0$$

Plane 1	Plane 2	Dihedral Angle (°)
1	2	1.16
1	3	85.56
1	4	83.91
3	4	1.64

Table 8.9

Bond Lengths and Angles Found in Barbituric Acid Derivatives

Average Length/Angle	Structure 1[282]	Structure 2[283]	Structure 3[284]	Structure 4[285]	Structure 5[286]	Structure 6[287]	Average of 6 Structures
C=O	1.216(10) Å	1.206(10) Å	1.217(5) Å	1.210(2) Å	1.212(4) Å	1.215(3) Å	1.213(6) Å
C-C	1.500(10)	1.480(10)	1.526(5)	1.518(2)	1.516(4)	1.523(3)	1.510(6)
C-N	1.367(10)	1.369(10)	1.373(5)	1.374(2)	1.369(4)	1.372(3)	1.371(6)
C-C-C	115.8(7)°	114.0(4)°	113.7(4)°	114.2(1)°	114.2(3)°	113.2(2)°	114.2(4)°
C-C-N	118.0(7)	118.0(4)	117.6(4)	118.3(1)	118.4(3)	118.9(2)	118.2(4)
C-N-C	125.5(7)	126.4(4)	125.1(4)	126.4(1)	126.2(3)	126.6(2)	126.0(4)
N-C-N	118.0(7)	115.1(4)	118.1(4)	116.3(1)	116.2(3)	115.3(2)	116.5(4)
C-C-O	122.8(7)	121.4(4)	120.2(4)	121.6(1)	121.6(3)	121.3(2)	121.5(4)
N-C-O	120.0(7)	121.1(4)	121.6(4)	120.7(1)	120.9(3)	121.0(2)	120.9(4)

Table 8.10

Bond Lengths and Angles Found in the Glycinato Rings

BOND LENGTHS

Ring I			Ring II				
Atom 1	Atom 2	Length(Å)	Atom 1	Atom 2	Length(Å)	Difference Ring I & II	Average Value
Mo	O3	1.991(5)	Mo	O4	2.024(4)	+0.033(4)	2.008(4)
O3	C2	1.325(8)	O4	C4	1.294(7)	-0.031(8)	1.310(8)
C2	C1	1.498(9)	C4	C3	1.530(9)	+0.032(9)	1.514(9)
C1	N1	1.486(8)	C3	N1	1.477(8)	-0.009(8)	1.482(8)
N1	Mo	2.337(5)	N1	Mo	2.337(5)	0.000(5)	2.337(5)
C2	O7	1.233(8)	C4	O6	1.221(7)	-0.012(8)	1.227(7)

Table 8.10

BOND ANGLES

Ring I				Ring II					
Atom 1	Atom 2	Atom 3	Angle(°)	Atom 1	Atom 2	Atom 3	Angle(°)	Difference Ring I & II°	Average Value°
Mo	O3	C2	121.4(4)	Mo	O4	C4	120.5(4)	-0.9(4)	121.0(4)
O3	C2	C1	116.8(6)	O4	C4	C3	116.8(5)	0.0(5)	116.8(5)
C2	C1	N1	109.5(5)	C4	C3	N1	107.2(5)	-2.3(5)	108.4(5)
C1	N1	Mo	105.6(3)	C3	N1	Mo	103.4(3)	-2.2(5)	104.5(3)
N1	Mo	O3	74.1(2)	N1	Mo	O4	74.0(2)	-0.1(2)	74.0(2)
O3	C2	O7	121.0(6)	O4	C4	O6	122.6(6)	1.6(6)	121.8(6)
C1	C2	O7	122.2(6)	C3	C4	O6	120.6(6)	-1.6(6)	121.4(6)

Σ(Internal Angles for Ring I) = 527.4°

Σ(Internal Angles for Ring II) = 521.9°

consequently weaker. In this structure the presence of a cis-dioxo group not only means less concentration of the π-bonding but also allows the carboxylato oxygen atoms to take up a trans positioning where they are not directly competing with the terminal oxygen atoms for the available empty d orbitals. Thus it would be expected that the bonds formed between molybdenum(V) and the carboxylato oxygen atoms in this structure would be stronger than those formed between molybdenum(VI) and the carboxylato oxygen atoms in the EDTA structure[1].

In the glycinato rings the bond angles about the nitrogen and methylene carbon atoms show only small variations from their ideal values while the sum of the angles subtended at each carboxylato carbon atom is 360.0° showing that these groups are planar, as expected.

The fact that the glycinato group resists unduly large folding and puckering has been well established by previous workers (see reference 1 and references contained therein) and is supported by the observation that the difference in the M-N and M-O bond lengths is large (0.15 to 0.35Å) whenever the M-O bond distance is large[281]. The difference in the lengths found here are 0.346Å and 0.313Å for the two carboxylate oxygen atoms. The difference to be expected on the grounds of the size differences is only 0.04Å [281] and the extra difference is caused by the resistance of the ring to undue puckering and folding.

A comparison of the internal bond angles in the two glycinato chelate rings reveals that those in ring II are, in every case, as small as or smaller than those found in ring I.

The cumulative effect of these differences is to make the sum of the interior angles in ring II only 521.9° and for ring I 527.4°. An angle of 540° would be expected for a planar conformation. A consequence of this is that ring II must display more pronounced out of plane distortions than ring I. The data listed in table 8.8 are for the displacements of the atoms in rings I and II from their respective mean planes and show that the average deviation from these mean planes is 0.075Å for ring I and 0.132Å for ring II. Another aspect to be taken into account is that the trans positioning for the O_c atoms of the glycinato rings calls for greater out-of-plane distortions of the rings than does the cis arrangement[1]. This is largely because the dihedral angle between either of the planes containing a ring C-N bond and the plane in which the trans Mo-O_c bonds ideally would lie to close both rings is 30° while the corresponding angle for the cis arrangement is only 15° [1]. The O_c-Mo-O_c angle found in this compound of 147.1(2)° agrees well with the value of 145° calculated using an averaged bite (2.73Å) found in aminepolycarboxylate ligands and complexing bond lengths found in the cis Mo(VI) EDTA complex[1]. It is said that redistribution and minimization of strain would probably call for some reduction in the bite in the trans case and this is what has been observed here where the bites are 2.621(8) and 2.635(8)Å for rings I and II respectively.

It is of interest here to note that the sterically less favourable configuration has been adopted for the glycinato rings. Assuming a cis arrangement for the terminal oxygen atoms two choices remain for the configuration of the glycinato rings. A cis arrangement (the sterically more favourable configuration) would lead to a molecule in which the oxygen

atom of one of the glycinato rings would be trans to a terminal oxygen atom, while the trans arrangement allows the two weaker donors (carbonyl oxygen and tertiary nitrogen atoms) to be trans to the terminal oxygen atoms. Evidence from this structure suggests that it is energetically more favourable to have the weakest π donors trans to the terminal oxygen atoms than to have a sterically more favourable geometry. This is further evidence for the generalization that in molybdenum(V) and (VI) stereochemistries the weakest donor atoms will be found trans to the terminal oxygen atom.

Since the ligand molecule is basically a substituted barbituric acid moiety and since there have been a number of structural characterisations of these types of molecules[282-287] an analysis of the bond lengths and angles of the pyrimidine ring should show to what extent the coordination of the pyrimidine carbonyl oxygen atom to molybdenum has distorted the electronic arrangement of the ring. Table 8.9 gives the relevant bond lengths and angles found in other barbiturate structures. It can be seen, from a comparison of the average values presented in table 8.9 with the values found in this structure, that there are a number of significant differences in both bond lengths and bond angles. The first such difference is between the lengths of the C-O bonds. In substituted barbituric acids these lengths range from 1.206-1.217Å with a mean value of 1.213(6)Å whereas the values found in this particular case are 1.246(7), 1.244(7) and 1.286(7)Å (this latter value for the C-O bond where the oxygen atom is coordinated to the molybdenum). Another significant difference is in the lengths of the carbon carbon bonds. In other

substituted barbituric acids these lengths have ranged from 1.48(1) to 1.526(5)Å with a mean value of 1.510(6)Å whereas the values found in the complex of 1.371(8) and 1.409(8)Å indicate considerable double bond character as does the increase in the C(6)-C(5)-C(7) angle from an average value of 114.2(4)° to 120.7(5)°. These differences indicate considerable electron delocalization around the pyrimidine ring with less localization of the π electrons in the C=O bonds.

In other structural determinations of substituted barbituric acid derivatives the pyrimidine ring has been found to be planar within statistical limits of error. The planarity of the pyrimidine ring has been preserved in this complex (see table 8.8) and indeed the atoms N(1), Mo, O(1) and O(2) have only small displacements of -0.03, 0.06, 0.11 and 0.14Å respectively from the mean plane defined by atoms O(8), O(9), N(2), N(3), C(7) and C(8). This suggests considerable electronic interaction between the <u>cis</u> MoO_2^+ group and the pyrimidine ring.

CHAPTER 9

THE MOLECULAR STRUCTURE OF $K_3[MoO_3(N(CH_2COO)_3)].H_2O$

9.1 INTRODUCTION

The solution of this structure was undertaken in part to characterise further the MoO_3 group (only two previous determinations have been made[1,6]) and also to enable the geometry of the ligand and its mode of attachment to be determined. There are two possible tridentate arrangements; either three oxygen donors or two oxygen donors and a nitrogen donor. Also it had been suggested[1] that it was both stereochemically and energetically plausible for the ligand to use all four of its donor atoms to give a seven coordinate structure.

It has been found that in aqueous solution at pH values between 3 and 8 the anionic species gives a single NMR signal attributable to the methylene protons[235]. With a view to confirming results obtained in the infrared study of this compound (that a cis trioxo molybdenum(VI) group was present) and that the coordination about the molybdenum atom was 6-fold rather than 7-fold, the structural determination of this compound was carried out.

9.2 EXPERIMENTAL SECTION

The compound $K_3[MoO_3NTA].H_2O$ is prepared by dissolving MoO_3 in a solution of NTA and adding the stoichiometric quantity of KOH. Transparent crystals were obtained on addition of ethanol and standing in a cold room for 3-4 days. The crystals so obtained were needles elongated in the direction of the c axis.

Crystallographic Data

$C_6H_8O_{10}NMoK_3$, MW = 467.4, is monoclinic with $\underline{a}$ = 9.700(2), $\underline{b}$ = 19.628(2), $\underline{c}$ = 7.608(1)Å, β = 110.58(2)°, $\underline{U}$ = 1352.5Å^3; D_m = 2.28(1) gm.cm^{-3}, D_c = 2.30 g.cm^{-3}, z = 4, F(000) = 920, μ = 19.05 cm^{-1} for MoKα.

Systematic absences occurred for the $o\underline{k}o$ reflections when $\underline{k}$ was odd and for the $h\underline{o}\ell$ reflections when ℓ was odd uniquely determining the space group as $\underline{P}\ 2_1/\underline{c}$. Unit cell dimensions and their esd's were obtained by least squares refinement of the setting angles of twelve reflections accurately centred in a 3.5 mm diameter circular receiving aperture in the manner given by Busing[266] and outlined more fully in chapters 6 and 7. The experimental density was determined by a pycnometric method using the liquids dibromoethane and dibromomethane.

Diffraction data were obtained from a crystal whose shape approximated that of an elongated irregular pentagonal bipyramid with bounding faces defined by the forms {010},{$\bar{1}$20}, {$\bar{1}\bar{2}$0}, {1$\bar{2}$0}, {120}, {$\bar{1}$02} and {101}. Crystal dimensions normal to these faces were 0.06, 0.06, 0.06, 0.06, 0.08, 0.14 and 0.12 mm respectively. A preliminary mosaicity check of the crystal showed that the width at half height of intense low angle reflections was acceptably low at 0.08°. Intensity data were recorded as described in chapters 6 and 7. A total of 3260 reflections was collected, and after editing and averaging of equivalent forms there was a total of 2652 independent reflections of which 1878 had intensities greater than 3σ(I) and 399 were considered as unobserved as they had intensities less than σ(I). Absorption corrections were applied before the final refinement and the transmission factors ranged from 0.61 to 0.81 for the 020 and 202 reflections respectively.

9.3 SOLUTION OF THE STRUCTURE AND REFINEMENT

The position of the molybdenum atom was located from a consideration of the Harker peaks obtained from a calculation of the Patterson function. After placing this atom in its calculated position and refining temperature and scale factors, values of 0.45 and 0.52 were obtained for R_1 and R_2. Positions for the three potassium atoms were obtained from an ensuing difference map and when these atoms were included in a structure factor calculation, values for R_1 and R_2 of 0.28 and 0.36 were obtained. A further difference map revealed the positions of all atoms in the nitrilotriacetate group and refinement of both positional and thermal parameters for all atoms lowered R_1 and R_2 to values of 0.096 and 0.132 respectively.

At this stage a difference map gave indications of anisotropy in the thermal motions of the heavier atoms and also revealed the presence of a peak which was assigned as an oxygen atom from the water molecule. Accordingly the molybdenum and three potassium atoms were allowed to vibrate anisotropically and the oxygen atom of the water molecule was included in the calculations. Values of 0.053 and 0.066 for R_1 and R_2 were obtained. At this point an analysis of the weighting scheme used revealed that the minimised function showed no systematic dependence on $|F_0|$ or $\sin \theta/\lambda$.

Positions of the hydrogen atoms were calculated on the basis of tetrahedral geometry with TETRIG and checked against a calculated difference Fourier, and in all cases these positions coincided with regions of high positive electron density. Accordingly the hydrogen atoms were included in their

calculated positions and assigned an isotropic temperature factor of 5.0 $\AA^3$ but neither positional nor thermal parameters were refined. Values of 0.053 and 0.070 for R_1 and R_2 were obtained.

Absorption corrections were applied and following refinement of temperature and scale factors values of R_1 and R_2 dropped to 0.045 and 0.058 respectively. Further refinement of all parameters including all reflections with intensities greater than $\sigma(I)$ gave values of R_1 and R_2 of 0.055 and 0.059 for 2234 reflections. A structure factor calculation using all weak and unobserved reflections not included in the refinement process revealed no anomalies of the type $F_c >> F_o$. A final difference map was calculated in which the highest peaks were only 1.0 $\bar{e}/\AA^3$, a value which is only one tenth the height of the peak for the last atom placed in the calculation. At this point the refinement was considered to be converged as the shifts were all less than one hundredth the value of the esd's for any parameter. Table 9.1 lists the positional and thermal parameters for the structure whilst table 9.2 lists the parameters for the hydrogen atoms. Table 9.3 gives the root mean square components of atomic thermal displacements. A structure factor listing for all 2234 reflections used in the final refinement is included in appendix J.

9.4 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of an assemblage of potassium cations, $[MoO_3NTA]^{3-}$ anions and water molecules. The $[MoO_3NTA]^{3-}$ anions and the water molecules are interconnected

Table 9.1

Positional and Thermal Parameters for the Molybdenum NTA Complex

Atom	X	Y	Z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.17533(6)	0.05613(3)	-0.10060(7)	0.00337(7)	0.00101(2)	0.0057(1)	-0.00015(3)	0.00129(6)	-0.00009(3)
K1	0.2818(2)	-0.02124(8)	0.3644(2)	0.0007(2),	0.00181(5)	0.0095(3)	0.00010(8)	0.0027(2)	0.00017(9)
K2	-0.1823(2)	0.22800(9)	-0.36656(2)	0.0074(2)	0.00197(5)	0.0133(4)	0.00050(9)	0.0006(2)	0.0013(1)
K3	0.0101(2)	0.10562(8)	-0.6014(2)	0.0064(2)	0.00140(4)	0.0092(3)	0.00017(7)	0.0020(2)	0.00008(9)
O1	0.2841(5)	-0.0146(2)	-0.0069(7)	2.23(9)					
O2	0.1295(5)	0.0839(2)	-0.9116(6)	1.90(8)					
O3	0.0140(5)	0.0260(2)	0.7295(7)	2.04(9)					
O4	0.2703(5)	0.0613(2)	-0.3197(6)	1.86(8)					
O5	0.1016(5)	0.1594(2)	0.7743(6)	1.75(8)					
O6	0.4602(6)	0.0860(3)	-0.4059(9)	2.56(9)					
O7	0.1030(6)	0.2681(3)	-0.1406(8)	3.2(1)					
O8	0.6248(6)	0.2120(3)	-0.7556(8)	3.1(1)					
O9	0.7296(6)	0.1189(3)	0.3992(7)	2.43(9)					
O10	0.8480(6)	0.1421(3)	-0.9774(8)	3.5(1)					

Table 9.1

Atom	X	Y	Z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N1	0.3771(6)	0.1342(3)	-0.9945(7)	1.19(9)					
C1	0.3105(8)	0.1995(4)	0.0345(9)	1.9(1)					
C2	0.1601(8)	0.2108(4)	-0.124(1)	2.0(1)					
C3	0.4492(8)	0.1422(4)	0.8616(9)	2.0(1)					
C4	0.3920(7)	0.0929(4)	0.7021(9)	1.6(1)					
C5	0.4865(7)	0.1078(4)	-0.8161(9)	1.8(1)					
C6	-0.13764(7)	0.1506(4)	-0.7203(9)	1.7(1)					

Table 9.2

Positional and Thermal Parameters (calculated) for Hydrogen Atoms

Atom	X	Y	Z	B
H1	0.5221	0.0582	0.1533	5.0
H2	0.4298	0.1007	0.2814	5.0
H3	0.3870	0.2401	0.0364	5.0
H4	0.2098	0.2075	-0.0830	5.0
H5	0.3784	0.1716	-0.0860	5.0
H6	0.5546	0.1356	-0.0254	5.0

Table 9.3

Root Mean Square Amplitudes of Vibration for the Molybdenum NTA Complex

Atom	Displacement Along X(Å)	Displacement Along Y(Å)	Displacement Along Z(Å)
Mo	0.115(1)	0.126(1)	0.142(1)
K1	0.152(3)	0.156(3)	0.188(3)
K2	0.158(3)	0.174(3)	0.237(3)
K3	0.150(3)	0.164(3)	0.173(2)

by hydrogen bonds. The anion is shown in figure 9.1 which also shows the numbering scheme for the atoms. Tables 9.4 and 9.5 give a listing of the bond lengths and bond angles found in the anion. The three donor atoms of the NTA ligand occupy the three vertices of one face of a distorted octahedron and the two glycinato rings are mutually cis (cf., $[MoO_2UDA]^-$ in chapter 7 where the two glycinato rings are mutually trans). The three vertices of the opposite face are occupied by the terminal oxygen atoms of the MoO_3 moiety.

The bond angles and distances found in the MoO_3 moiety in the anion are similar to those found in other compounds containing this group[1,6] (see table 9.6). As can be seen from a comparison of the values found in this case with those found for dioxo groupings (see tables 7.8 and 8.7), the molybdenum oxygen bond length is significantly longer in the trioxo case reflecting the fact that the three oxygen atoms are competing for the available π orbitals on the molybdenum atom. This lengthening is also reflected in the lowering of the molybdenum oxygen stretching force constant as $\nu(Mo\text{-}O_t)$ for the trioxo case is in the 800-900 cm^{-1} region while for the dioxo case it is found in the 900-950 cm^{-1} region.

In further discussion of the complex anion it is convenient to use O_o to designate any of the three oxide oxygen atoms (O(1) O(2) and O(3)) of the MoO_3 moiety and either O_c, O_u or O_f for the carboxylate oxygen atoms depending on whether these are coordinated to the molybdenum atom (O(4), O(5)), not attached to the molybdenum (O(6), O(7)), or whether they exist in a "free" carboxylate grouping (O(8), O(9)).

It has been postulated that a seven coordinate molybdenum(VI) complex of NTA is "both stereochemically and

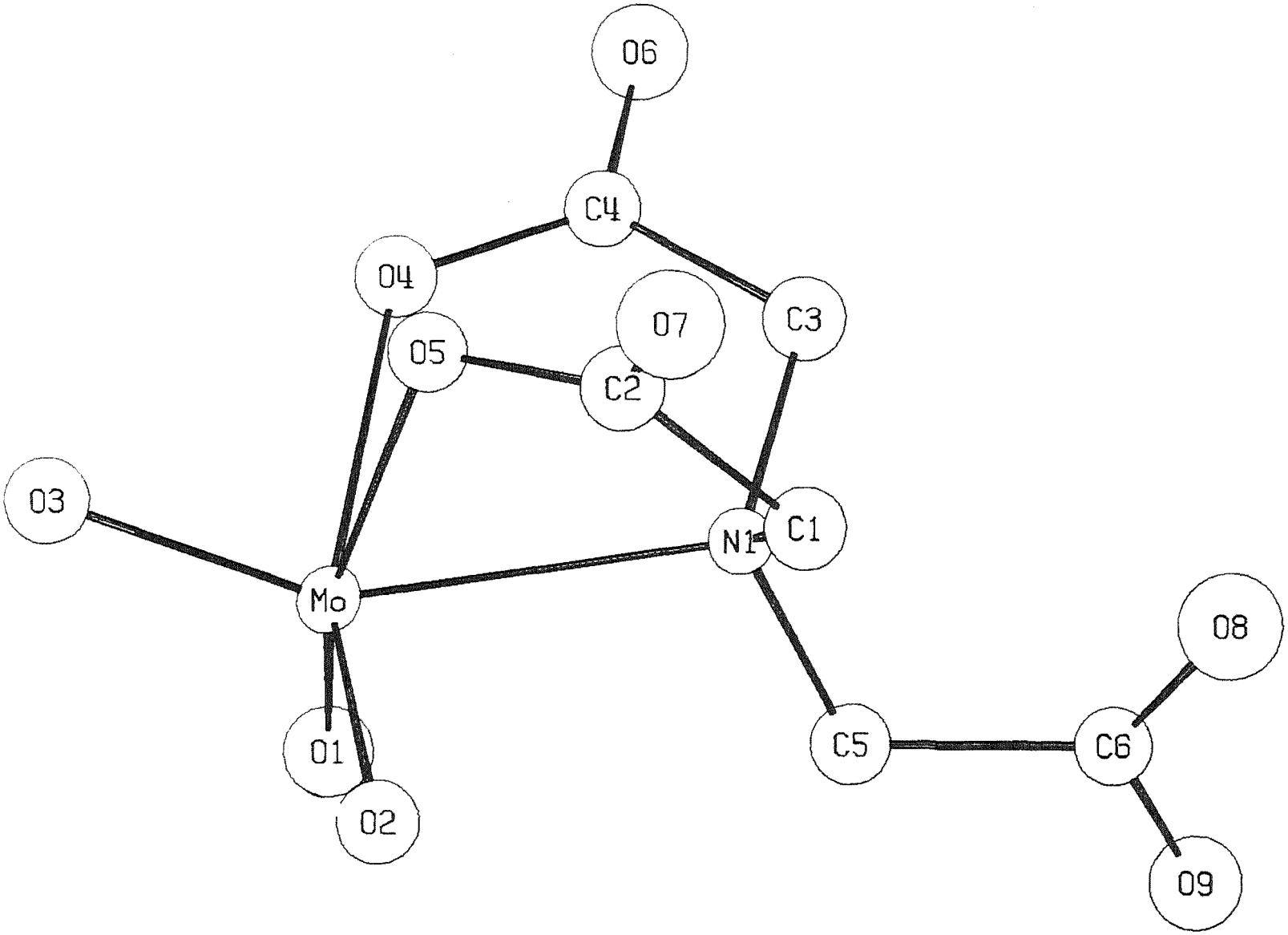


Figure 9.1 Structure of the Molybdenum NTA Anion

Table 9.4

Bond Lengths in the $[MoO_3NTA]^{3-}$ Anion

Atom 1	Atom 2	Length(Å)
Mo	O1	1.735(5)
Mo	O2	1.737(4)
Mo	O3	1.737(5)
Mo	O4	2.176(4)
Mo	O5	2.245(5)
Mo	N1	2.388(5)
O4	C4	1.291(8)
O5	C2	1.276(8)
O8	C6	1.234(8)
O6	C4	1.233(8)
O7	C2	1.239(9)
O9	C6	1.266(8)
C1	C2	1.540(9)
C3	C4	1.494(9)
C5	C6	1.520(9)
C1	N1	1.486(8)
C3	N1	1.503(8)
C5	N1	1.485(8)

Table 9.5

Bond Angles in the $[MoO_3NTA]^{3-}$ Anion

Atom 1	Atom 2	Atom 3	Angle(°)	Atom 1	Atom 2	Atom 3	Angle(°)
O1	Mo	O2	102.1(2)	Mo	N1	C1	104.8(2)
O1	Mo	O3	106.6(2)	Mo	N1	C3	111.0(2)
O1	Mo	O4	89.4(2)	Mo	N1	C5	108.4(2)
O1	Mo	O5	162.1(2)	O4	C4	C3	118.2(6)
O1	Mo	N1	94.1(2)	O5	C2	C1	116.9(6)
O2	Mo	O3	107.1(2)	O8	C6	C5	120.6(6)
O2	Mo	O4	157.3(2)	O9	C6	C5	114.7(6)
O2	Mo	O5	86.0(2)	O4	C4	O6	123.0(6)
O2	Mo	N1	86.6(2)	O5	C2	O7	124.7(7)
O3	Mo	O4	87.8(2)	O8	C6	O9	124.6(6)
O8	Mo	O5	85.8(2)	O6	C4	C3	118.8(6)
O3	Mo	N1	151.7(2)	O7	C2	C1	118.4(6)
O4	Mo	O5	77.9(2)	C1	N1	C3	111.1(5)
O4	Mo	N1	73.1(2)	C1	N1	C5	111.8(5)
O5	Mo	N1	70.2(2)	C3	N1	C5	109.6(5)
Mo	O4	C4	122.8(2)	C4	C3	N1	113.0(6)
Mo	O5	C2	116.9(2)	C2	C1	N1	110.4(5)

energetically plausible"[1] although it can be seen from this structure that normal six-fold coordination occurs with the extra glycinato group not being attached to the molybdenum atom. From the diagram (figure 9.1) it can be seen that the three oxygen atoms O_o and three donor atoms of the NTA ligand are arranged in a stereochemistry approaching that of a trigonal pyramid rather than that of a regular octahedron. This trigonal pyramidal geometry for the MoO_3 moiety must be accompanied by the observed cis positioning of the complexing O_c atoms in the coordination sphere, and that trans positioning of either of two O_o atoms or of the two O_c atoms automatically demands trans positioning of the other pair. The cis geometry observed here is the most favourable as it allows both the glycinato rings to be mutually cis (a geometry which has been shown to be the most favourable stereochemically) and the three O_o atoms to be mutually cis, a configuration which has been shown to be the most favourable as it allows maximum utilization of the molybdenum π orbitals (see chapter 2).

The molybdenum oxygen bond lengths to the donor atoms of the NTA group (2.176(4) and 2.245(5)Å) are significantly longer than the corresponding lengths (1.991(5) and 2.024(4)Å) found in the $[MoO_2UDA]^-$ anion (see chapter 8) but this merely reflects the trans effect of the molybdenum terminal oxygen atoms. The bonds are similar in length to those found in the $[(MoO_3)_2EDTA]^{4-}$ anion where the trans effect also applies, values of 2.176(6) and 2.213(6)Å being found[1]. The molybdenum nitrogen bonds are of similar length in all four structures as these all lie trans to molybdenum terminal oxygen atoms. The actual values are 2.332(9)Å in MoO_3 dien[6], 2.337(5)Å in $[MoO_2UDA]^-$, 2.388(5)Å in $[MoO_3NTA]^{3-}$, and 2.399(6)Å in

$[(MoO_3)_2EDTA]^{4-}$.[1]

The presence of both complexed and uncomplexed glycinato groups in this molecule makes it possible to determine the extent of the distortions imposed on this group by chelation. Table 9.7 gives bond parameters for the three glycinato groups. Considerable distortions from normal bond lengths and angles have occurred, especially for the C-C and C-N bonds. However, even in the "free" glycinato ring the two carbon oxygen bond lengths do not appear to be equal. There appears to be no crystallographic reason why these should not be equivalent as neither of the oxygen atoms is involved in any hydrogen bonding and the closest intermolecular contact is 3.496(8)Å between O(9) and O(6) (see table 9.9 for inter- and intramolecular contact distances).

The difference between $C-O_c$ and $C-O_u$ bond lengths found here is greater than that found in the case of the $[(MoO_3)_2EDTA]^{4-}$ [1] anion but less than that for for the $[MoO_2UDA]^-$ anion (see chapter 8). This indicates that the order of strength of the $Mo-O_c$ bond is $[MoO_2UDA]^- > [MoO_3NTA]^{3-} > [(MoO_3)_2EDTA]^{4-}$. The magnitudes of the differences between the $C-O_c$ and $C-O_u$ bonds in the three cases are 0.092(16) and 0.073(14), 0.058(16) and 0.037(17), 0.019(18) and 0.032(16)Å respectively. However, as discussed above, the $Mo-O_c$ bonds in the $[MoO_2UDA]^-$ are not found <u>trans</u> to $Mo-O_o$ bonds and therefore would be expected to be stronger than similar bonds found in $[MoO_3NTA]^{3-}$ and $[(MoO_3)_2EDTA]^{4-}$. The greater strength of the $Mo-O_c$ bonds in the $[MoO_3NTA]^{3-}$ anion, over those in the $[(MoO_3)_2EDTA]^{4-}$ anion, explains in part the greater distortions imposed on the glycinato rings found in the $[MoO_3NTA]^{3-}$ anion. These distortions show up in a comparison of the values of the

Table 9.6

Angles and Distances found in Molybdenum Trioxo Structures

Parameter	Parameters for $[MoO_3Den]^{4\ 1}$	Parameters for $[(MoO_3)_2EDTA]^{4\ 1}$	Parameters for $[MoO_3NTA]^{3-}$
Mo-O1*	1.735(6)	1.731(6)	1.735(5)
Mo-O2*	1.735(6)	1.749(6)	1.737(4)
Mo-O3*	1.739(8)	1.739(6)	1.737(5)
O1-Mo-O2*	105.3(3)	104.9(3)	102.1(2)
O1-Mo-O3*	106.8(3)	107.5(3)	106.6(2)
O2-Mo-O3*	105.3(3)	104.5(3)	107.1(2)

*Numbering scheme based on model

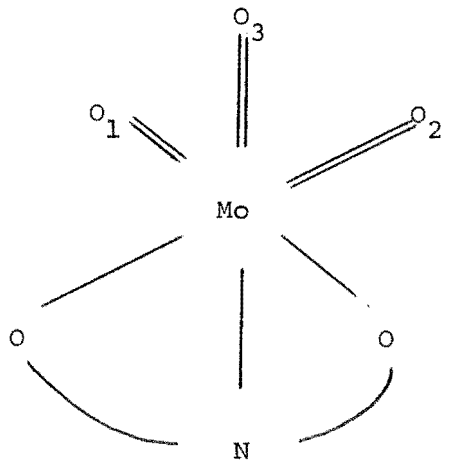


Table 9.7

Bond Parameters for the Glycinato Rings

Bond Parameter[a]	Glycinato Group 1[b]	Glycinato Group 2[c]	Glycinato Group 3[d]
Lengths	Lengths Å	Lengths Å	Lengths Å
Mo-O1	2.176(4)	2.245(5)	-
O1-C1	1.291(8)	1.276(8)	1.234(8)
C1-O2	1.233(8)	1.239(9)	1.266(8)
C1-C2	1.494(9)	1.540(9)	1.520(9)
C2-N1	1.503(8)	1.486(8)	1.485(8)
Mo-N1	2.388(5)	2.388(5)	-
Angles	Angles(°)	Angles(°)	Angles(°)
Mo-O1-C1	122.8(2)	116.9(2)	-
O1-C1-C2	118.2(6)	116.9(6)	120.6(6)
O1-C1-O2	123.0(6)	124.7(7)	124.6(6)
O2-C1-C2	118.8(6)	118.4(6)	114.7(6)
C1-C2-N1	113.0(6)	110.4(5)	117.5(6)
C2-N1-Mo	111.0(2)	104.8(2)	-
N1-Mo-O1	73.1(2)	70.2(2)	-
	Σ internal angles = 535.1	Σ internal angles = 519.2	

(b) Consisting of atoms Mo, O4, C4, O6, C3, N1

(c) Consisting of atoms Mo, O5, C2, O7, C1, N1

(d) Consisting of atoms N1, C5, C6, O8, O9

(a) Numbering scheme referring to diagram

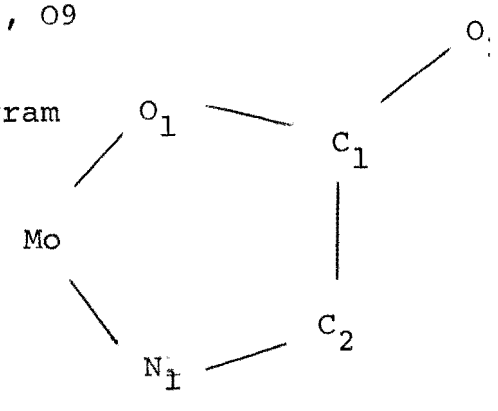


Table 9.8

Results of Mean Plane Calculations

Mean Plane 1: Glycinato Ring 1

Atom	Deviation from Least Squares Plane (Å)	e.s.d. for Atom (Å)
Mo	0.0048	0.0006
O4	-0.420	0.005
C4	-0.293	0.007
C3	0.274	0.007
N1	0.133	0.005
Other Atoms	Distance from Plane (Å)	e.s.d. (Å)
O6	-0.962	0.006

Equation of Plane 1

$$-0.8312X + 0.2373Y - 0.5027Z + 1.0213 = 0$$

Mean Plane 2: Glycinato Ring 2

Atom	Deviation from Least Squares Plane (Å)	e.s.d. for Atom (Å)
Mo	0.0006	0.0006
O5	-0.068	0.005
C2	0.874	0.008
C1	-0.598	0.008
N1	-0.094	0.006
Other Atoms	Distance From Plane (Å)	e.s.d. (Å)
O7	1.623	0.006

Equation of Plane 2

$$-0.5072X + 0.8455Y - 0.1669Z - 0.0455 = 0$$

Angle between planes 1 and 2 = 45.08°.

Table 9.9

Intermolecular and Intramolecular Nonbonding Contracts (<3.5Å)

Intramolecular			Intermolecular		
Atom 1	Atom 2	Length(Å)	Atom 1	Atom 2	Length(Å)
Mo	C2	3.042(8)	O1	C3	3.484(8)
O1	O2	2.700(8)	O2	O3	3.146(8)
O3	O4	2.732(8)	O5	O7	3.467(8)
O4	O6	2.219(8)	O6	C5	3.250(8)
O5	O7	2.228(8)	O9	O6	3.496(8)
O8	O9	2.213(8)			
O10	O5	3.358(8)			
N1	C2	2.485(8)			
C1	O7	2.392(8)			
C2	N1	2.485(8)			
C3	O6	2.351(8)			
C4	N1	2.499(8)			
C5	O9	2.350(8)			
C6	N1	2.569(8)			

Hydrogen Bond Lengths & Angle

Atom 1	Atom 2	Length(Å)
O10	O2	2.797(8)
O10	O1	2.856(8)

Atom 1	Atom 2	Atom 3	Angle(°)
O1	O10	O2	92.0(2)

C-C and C-N bond lengths and bond angles found in the glycinato rings and in the deviations from planarity of these rings. Values of these parameters for ring 1 show the most distortion from ideal values corresponding to the fact that the Mo-O_c bond in ring 1 is stronger (shorter) than that found in ring 2 (as seen from both the differences between C-O_c and C-O_u bond lengths and the differences between the two Mo-O_c bond lengths).

The sums of the internal angles for the two rings shows that in ring 2 there must be considerable deviations from planarity. These sums are 535.1° and 519.2° respectively for rings 1 and 2 (Σ(internal angles) = 540° for ideal plane). The magnitudes of the distortions found in the glycinato rings in the $[MoO_3NTA]^{3-}$ anion are in all cases greater than those found in the $[(MoO_3)_2EDTA]^{4-}$ anion reflecting the greater strength of the Mo-O_c bonds. In both rings the sums of the angles about the carboxylate carbon atoms are equal to 360.0° showing the planarity of this group.

The steric requirements of the chelating agent are best satisfied by the observed cis arrangement of bonds. The steric requirements of the MoO_3 moiety are better handled by the observed trigonal pyramidal geometry than with the octahedral geometry with an O_o-Mo-O_o angle of 90° and a Mo-O_o length of 1.74Å which leads to an O_o-O_o separation of only 2.46Å [1] much below the corresponding 2.70Å separation found in the trigonal pyramidal moiety.

The three potassium ions have oxygen atoms as nearest neighbours. The distances from the potassium ions range from 2.60 to 2.95Å (see table 9.10) while the nearest non-oxygen atom is 3.01Å from a potassium ion. One potassium ion,

Table 9.10

Coordination Environment for the Potassium Ions

Environment for K1			Environment for K2			Environment for K3		
Distances (Å)			Distances (Å)			Distances (Å)		
K1	O9	2658(5)	K2	O8	2.604(6)	K3	O7	2.690(6)
K1	O3	2.700(5)	K2	O9	2.705(6)	K3	O9	2.735(5)
K1	O6	2.722(5)	K2	O7	2.803(6)	K3	O3	2.742(5)
K1	O1	2.835(5)	K2	O10	2.889(6)	K3	O4	2.801(5)
K1	O6'	2.885(5)	K2	O5	2.894(6)	K3	O5	2.873(5)
K1	O4	2.934(5)	K2	O8'	2.896(6)	K3	O3'	2.952(5)
K1	O2	2.938(5)						
Angles(°)			Angles(°)			Angles(°)		
O9	K1	O3 81.7(2)	O8	K2	O9 118.7(2)	O7	K3	O9 106.6(2)
O9	K1	O6 81.0(2)	O8	K2	O7 109.6(2)	O7	K3	O3 144.9(2)
O9	K1	O1 136.4(2)	O8	K2	O10 85.1(2)	O7	K3	O4 97.2(2)
O9	K1	O6' 106.1(2)	O8	K2	O4 142.2(2)	O7	K3	O5 77.0(2)
O9	K1	O4 79.7(2)	O8	K2	O8' 95.8(2)	O7	K3	O3' 132.8(2)
O9	K1	O2 149.1(2)	O9	K2	O7 129.8(2)	O9	K3	O3 97.6(2)
O3	K1	O6 149.4(2)	O9	K2	O10 118.8(2)	O9	K3	O4 130.7(2)
O3	K1	O1 97.2(2)	O9	K2	O5 85.3(2)	O9	K3	O5 85.2(2)
O3	K1	O6' 122.4(2)	O9	K2	O8' 46.4(2)	O9	K3	O3' 76.0(2)
O3	K1	O4 83.5(2)	O7	K2	O10 76.9(2)	O3	K3	O4 85.3(2)
O3	K1	O2 67.7(2)	O7	K2	O4 46.0(2)	O3	K3	O5 131.0(2)
O6	K1	O1 78.6(2)	O7	K2	O8' 142.3(2)	O3	K3	O3' 77.2(2)
O6	K1	O6' 86.7(2)	O10	K2	O5 109.7(2)	O4	K3	O5 58.7(2)
O6	K1	O4 117.8(2)	O10	K2	O8' 78.1(2)	O4	K3	O3' 56.6(2)
O6	K1	O2 128.1(2)	O5	K2	O8' 120.8(2)	O5	K3	O3' 56.0(2)
O1	K1	O6' 110.7(2)						
O1	K1	O4 143.8(2)						
O1	K1	O2 55.7(2)						
O6'	K1	O4 44.8(2)						
O6'	K1	O2 87.7(2)						
O4	K1	O2 92.3(2)						

K1, has seven nearest neighbour oxygen atoms and the other two potassium ions have six oxygen atoms. The latter have these oxygen atoms arranged in a distorted octahedron while in the former case the smallest angle subtended at the potassium ion by the oxygen atoms is $44.8(2)^{\circ}$.

In this structure there are two contact distances with values ca. 2.8Å involving the water molecule. All other intermolecular contacts have values greater than 3.15Å (see table 9.9 for both hydrogen bond parameters and inter- and intramolecular contact distances). These contacts involving the water molecule are considered to be hydrogen bonds as there are two hydrogen atoms available for these bonds. The angle subtended at the water oxygen atom is $92.0(2)^{\circ}$, a value which is in variance with the H-O-H angle in an isolated water molecule of 104.5°. However it has been found that for hydrogen bonds involving the water molecule the O-O-O angle varies from $80\text{-}130^{\circ}$ [269]. The two hydrogen bonds from each water molecule involve two oxide atoms (O_o) in adjacent anions, the whole system making up a three dimensional network.

APPENDIX A

Bond Lengths Found in Structure Analyses of Molybdenum(V) and (VI) Compounds

The following abbreviations are used in the column headings: O_t - terminal oxygen atom; O_b - bridging oxygen atom; O_l - oxygen atom from ligand; N_l - nitrogen atom from ligand; S_l - sulphur atom from ligand; OH_2 - water molecule attached through an oxygen atom. All measurements are in Å, esd's are in parentheses.

Formulae	Mo-O_t	Mo-O_b	Mo-O_l	Mo-OH_2	Mo-N_l	Mo-S_l	Mo-Cl	Mo-Br	Mo-F	Reference Number
$[MoO_3(C_2O_4)]^{2-}$	1.815(4) 1.850(4)	2.230(4) 1.878(4)	2.235(4) 2.242(4)							22
$[MoO(O_2)_2(C_2O_4)]^{2-}$	1.68(1)		2.08(1) 2.26(1)							293
$MoO_2(C_5H_7O_2)_2$	1.69		1.98 2.19							44
$[MoO(O_2)_2OOH]_2^{2-}$	1.669(6)	2.047(6) 2.391(6)	1.938(6)							294
$[Mo_4O_{11}(C_4H_3O_5)_2]^{4-}$	1.72	1.88	2.30 2.00							14
$\{[MoO_2C_2O_4(H_2O)]_2O\}^{2-}$	1.69(1)	1.876(2)	2.08(2) 2.19(2)	2.33(2)						5
$[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$	1.66(1)	1.93(1)	1.95(1) 1.96(1) 1.97(1) 1.98(1)	2.45(1)						30
$MoO(O_2)_2(C_6H_{18}N_3PO)(H_2O)$	1.662(5)		2.057(5) 1.944(5)	2.347(5)						27
$\{[MoO(O_2)_2(H_2O)]_2O\}^{2-}$	1.674(7)	1.917(7)	1.963(1)	1.445(7)						294

Formulae	Mo-O_t	Mo-O_b	Mo-O_l	Mo-OH_2	Mo-N_l	Mo-S_l	Mo-Cl	Mo-Br	Mo-F	Reference Number
$\{[MoO(C_2O_4)(H_2O)]_2O_2\}$	1.70(3)	1.90(3)	2.12(3)	2.22(4)						29
$MoO_3(C_4H_{13}N_3)$	1.736(8)				2.324(7)					6
$[(MoO_3)_2(C_{10}H_{12}O_8N_2)]^{4-}$	1.740(6)		2.176(6) 2.213(6)		2.399(5)					1
$MoO_2(C_6H_{12}O_3N)$	1.79(4)		1.94(3) 2.34(4)		2.43(4)					26
$MoO_2(C_9H_6ON)_2$	1.71(2)		1.98(2)		2.32(2)					43
$MoO(O_2)_2(C_6H_{18}N_3PO)\cdot(C_5H_5N)$			2.04(1) 1.93(1)		2.45(1)					27
$[Mo(CN)_8]^{3-}$					1.16(2)					295
$Mo_2O_4(C_6H_9O_2N_3)_2$	1.71	1.92	2.21		2.24 2.21					182
$Mo_2O_3(C_3H_5OS_2)_4$	1.65(3)	1.86(3)				2.46(1) 2.51(1) 2.54(1) 2.70(1)				9
$MoO_2(C_5H_{10}NS_2)_2$	1.63(2)					2.443(8) 2.63(1)				189
$Mo_2O_4(C_5H_{10}O_2NS)_2$	1.67(2)	1.92(2)			2.24(2)	2.393(8)				18
$Mo_2O_2S_2(C_4H_8O_2NS)_2$	1.65(3)				2.23(3)	2.37(1) 2.30(1)*				34
$Mo_2O_4(C_3H_5O_2NS)_2$	1.71(2)	1.91(2) 1.95(2)	2.29(2)		2.26(2)	2.490(6)				10

Formulae	$Mo-O_t$	$Mo-O_b$	$Mo-O_l$	$Mo-OH_2$	$Mo-N_l$	$Mo-S_l$	Mo-Cl	Mo-Br	Mo-F	Reference Number
$Mo_2O_2S_2(C_6H_9O_2N_3)_2$	1.70(2)		2.24(2)		2.26(2) 2.20(2)	2.31(1)*				185
$Mo_2O_3(C_4H_{10}O_2PS_2)_4$	1.65(1)	1.86(1)				2.442(5) 2.547(5) 2.801(5)				295
$MoO_2Cl_2(C_3H_7ON)_2$	1.68(1)		2.20(1)				2.341(7)			41
$[MoOCl_5]^{2-}$	1.67(4)						2.40(2) 2.63(2)			21
$[MoOCl_4H_2O]^-$	1.72(5)						2.27(2) 2.35(2)			21
$MoO_2Cl_2H_2O$	1.65(4)	1.77(8) 2.20(8)		2.26(4)			2.34(1)			23
$MoO_2Cl_2(C_2H_6OS)_2$	1.64(1)		2.11(2) 2.23(2)				2.366(7) 2.432(7)			190
$MoOCl_3$	1.60(2)						2.28(1) 2.46(1)* 2.81(1)*			20
$MoCl_5$							2.24(1) 2.53(1)			33
$MoOBr_5$	1.86(3)							2.56(1) 2.83(1)		21
$[MoOBr_4H_2O]^-$	1.78(7)			2.39(3)				2.516(4)		35
$MoOBr_3$		1.65 2.31						2.41 2.61*		297
$MoO_2Br_2(C_{10}H_8N_2)$	1.64(2) 1.82(2)				2.26(2) 2.45(2)			2.461(3) 2.781(3)		4

*bridging

Formulae	Mo-O_t	Mo-O_b	Mo-O_l	Mo-OH_2	Mo-N_l	Mo-S_l	Mo-Cl	Mo-Br	Mo-F	Reference Number
$[MoO(O_2)F_4]^{2-}$	1.64(2)		1.94(2)						2.00(1) 2.03(3)	298
$[MoO_2F_4]^{2-}$	1.68(2) 1.73(1)								1.93(1) 2.00(1)	42
$[MoOF_5]^{2-}$	1.66(2)								1.88(2) 2.02(1)	31
$[MoO(O_2)F_4]^{2-}$	1.67(2)		1.91(1) 1.94(3)						2.03(1)	25
$[MoO_2F_3]^{-}$	1.68(6)								1.89(6) 2.11(1)*	32

APPENDIX B

Infrared Stretching Frequencies for Mo-O_t and Mo-X (X = F,Cl,Br) Bonds

All frequencies are quoted in cm^{-1}

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
Values for Molybdenum(V) Complexes					
$[MoO_2F_3]^{2-}$	951	898	554	440	47
$[Mo_2O_4(C_2O_4)_2(H_2O)_2]$	980				36,188,299
$MoO_2Cl(C_5H_5)$	920	887			300
$Mo_2O_5(C_5H_5)_2$	930	898			300
$[Mo_2O_4(C_{10}H_{12}O_8N_2)]^{2-}$	940				239
$MoOCl_3$	1020				40,53,68, 301
$[MoOCl_4]^-$	1000				69
$[MoOCl_5]^{2-}$	967		339	327	36,302,303
$[MoOBr_4]^-$	985				279
$MoOCl_3(C_{18}H_{15}PO)_2$	967		326	317	40,79,304
$MoOCl_3(C_{18}H_{15}AsO)_2$	967				79
$MoOCl_3(C_2H_6OS)_2$	967				40,79
$MoOCl_3(C_2H_3N)_2$	980				98
$MoOCl_3(C_3H_5N)_2$	980				98
$MoOCl_3(C_4H_7N)_2$	980				98
$MoOCl_3(C_{10}H_8N_2)$	975				98
$MoOCl_3(C_{12}H_8N_2)$	975				98,305
$MoOCl_3(C_{18}H_{15}P)_2$	950				98
$MoO(OH)_3$	977				305
$MoO_2Cl(C_{10}H_8N_2)$	952				305
$Mo_2O_3Cl_4(C_{10}H_8N_2)$	966				305
$[MoOCl_4C_2H_3N]^-$	990				306
$MoOCl_3(C_9H_7ON)$	935				279
$[MoO(NCS)_5]^{2-}$	945				2
$[MoO(CN)_4]^-$	929				279
$[Mo_2O_3(NCS)_8]^{4-}$	950				2
$Mo_2O_3(C_5H_7O_2)_4$	961				307
$Mo_2O_3(C_3H_5OS_2)_4$	946				36,217
$Mo_2O_3(C_9H_6ON)_4$	940				2
$[Mo_2O_4(NCS)_6]^{4-}$	952				308
$MoOCl_3(C_5H_8O_2)$	990				40

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$MoOCl_3(C_{13}H_{10}O)_2$	990				40
$MoOCl_3(C_5H_5N)_2$	966				40
$MoOCl(C_5H_7O_2)_2$	962				40
$Mo_2O_4Cl_2(C_{10}H_8N_2O_2)_2$	943				309
$Mo_2O_3Cl_4(C_{10}H_8N_2O_2)_2$	942				309
$[Mo_2O_4(C_2O_4)_2(C_5H_5N)_2]^{2-}$	960				188
$[Mo_2O_3(C_2O_4)_2(C_9H_6ON)_2]^{2-}$	970				188
$[Mo_2O_3(C_2O_4)_2(C_6H_4O_2N)_2]^{2-}$	973				188
$Mo_2O_3(C_2O_4)_2(C_{12}H_8N_2)_2$	965				188
$Mo_2O_3(C_3H_6NS_2)_4$	930				217
$Mo_2O_3(C_5H_{10}NS_2)_4$	930				217,310
$Mo_2O_3(C_2H_3OS_2)_4$	952				217
$Mo_2O_4(C_6H_9O_2N_3)_2$	941				180
$MoOBr_3(C_{26}H_{24}O_2P_2)$	965		247		234,304
$MoOCl_3(C_{26}H_{24}O_2P_2)$	973		315		234,304
$[MoOBr_5]^{2-}$	962		253	244	303
$Mo_2O_4Cl_2(C_{10}H_8N_2)_2$	952				311
$MoOF_3(C_{12}H_8N_2)$	980				312
$Mo_2O_3F_4(C_{10}H_8N_2)_2$	962				312
$Mo_2O_3(C_4H_8O_2NS)_4$	932				97
$Mo_2O_4(C_4H_8O_2NS)_2$	978				97
$Mo_2O_2S_2(C_4H_8O_2NS)_2$	966				97
$[Mo_2O_4(C_4H_8O_2NS)_2]^{2-}$	955				97
$[Mo_2O_2S_2(C_3H_5O_2S)_2]^{2-}$	948				97
$[Mo(CH_3O)_2Cl_4]^-$			300		313
$[Mo(C_2H_5O)_2Cl_4]^-$			306		313
$Mo_2O_3(H_2O_2P)_4$	965				314
$Mo_2O_4(H_2O_2P)(C_{10}H_8N_2)$	957				314
$Mo_2O_4(H_2O_2P)(C_{12}H_8N_2)$	957				314
$MoOCl_3(C_3H_2N_2)$	972				315
$MoOCl_3(C_4H_4N_2)$	988		328	317	315
$MoOCl_3(C_6H_8N_2)$	980		328	312	315
$MoOCl_3(C_4H_4N_2)$	989		355	325	315
$MoOCl_3(C_4H_4N_2)_2$	977				315
$MoOCl_3(C_8H_4N_2)$	981				315
$MoOCl_3(C_{10}H_8N_2)$	973				315
$MoOCl_3(C_{10}H_8N_2)_2$	976				315

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$Mo_2O_3(C_2H_3O_2)(C_5H_{10}NS_2)$	969				316
$Mo_2O_3(C_4H_{10}O_2S_2P)_4$	967				316
$Mo_2O_3(C_{12}H_{10}O_2S_2P)_4$	972				316
$Mo_2O_3(C_5H_{10}O_2NS)_4$	925				181
$Mo_2O_4(C_5H_{10}O_2NS)_2$	980				181
$MoOBr_3(C_{18}H_{15}OP)_2$	973		243		234,304
$Mo_2O_4Cl_2(C_{12}H_8N_2)_2$	955				317
$[MoOCl_3(C_5HO_2F_6)]^-$	976				70
$[MoOCl_3(C_5H_4O_2SF_3)]^-$	965				70
$[MoOCl_3(C_{10}H_6O_2F_3)]^-$	966				70
$[MoOCl_3(C_{15}H_{11}O_2)]^-$	956				70
$[MoOBr_3(C_{15}H_{11}O_2)]^-$	955				70
$MoOCl_3(C_4H_8O)_2$	985				318
$MoOCl_3(C_5H_{10}O)_2$	985				318
$MoOCl_3(C_4H_8O_2)$	985				318
$MoOCl_3(C_4H_8OS)$	990				318
$MoOCl_2(C_4H_{10}O_2)$	985				318
$Mo_2O_3(C_2H_5OS)_4$	950				97
$Mo_2O_4(C_2H_5OS)_2$	956				97
$MoOCl_3(C_{10}H_{16}As_2)$	956	932			66
$MoOCl_3(C_{26}H_{24}P_2)$	941				67
$MoO(OH)(C_{44}H_{30}N_4)$	902				319
$MoOCl(C_{44}H_{30}N_4)$	941				319
$MoO(OOH)(C_{44}H_{30}N_4)$	900				319
Values for Molybdenum(VI) Complexes					
$[MoO_2F_4]^{2-}$	951	920	549	441	47
$[MoO_2F_5]^{3-}$	953	887	538	440	47
$[MoO_3F_2]^{2-}$	910	850	452	440	47
$[Mo_2O_4F_7]^{3-}$	967	919	560	463	47
$[Mo_4O_{13}F]^{3-}$	947	899	555	459	47,320
$[Mo_3O_6F_{11}]^{5-}$	959	894	554	435	47
$[MoO_2Cl_4]^{2-}$	960	922			47
$[MoO_3(C_2O_4)]^{2-}$	903	869			47
$MoO_3(C_4H_{13}N_3)$	876	825			47
$[MoO(O_2)Cl_4]^{2-}$	933	918	322	304	321
$[MoO(O_2)F_4]^{2-}$	972	953	501		321
$[MoO(O_2)_2F_2]^{2-}$	938		518	493	321

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$[MoO_2(O_2)(C_2O_4)(H_2O)]^{2-}$	912	894			321
$MoOCl_4$	1015		450	396	40,53,217, 239,322-4
MoO_3	992				302
$MoO_2Cl_2(C_8H_8O)_2$	957	914			223
$[MoO_2(C_2O_4)_2]^{2-}$	903				279
$[MoO_2(C_6H_4O_2)_2]^{2-}$	895				279
$MoO_2(C_5H_7O_2)_2$	935	905			325
$[Mo_2O_5(C_2O_4)(H_2O)_2]^{2-}$	960	920			36
$[MoO_3(C_2O_4)H_2O]_n^{2n-}$	880	837			2
$[(MoO_3)_2(C_{10}H_{12}O_8N_2)]^{4-}$	900	840			239
$MoO_2(C_3H_6NS_2)_2$	908	873			36,217
$MoO_2Cl_2(C_3H_7ON)_2$	939	905			40
$MoO_2Cl_2(C_4H_9ON)_2$	948	909			40
$MoO_2Cl_2(C_{10}H_{21}ON)_2$	943	909			40
$MoO_2Cl_2(C_{10}H_8N_2)$	935	906			80,224
$MoO_2Br_2(C_{10}H_8N_2)$	934	903	253		80,224
$MoO_2(C_5H_{10}NS_2)_2$	905	877			217,310
$MoO_2(C_7H_{14}NS_2)_2$	909	875			217
$MoO_2(C_9H_{18}NS_2)_2$	909	877			217
$MoO_2Br_2(C_4H_8O)$	966	924			224
$MoO_2Br_2(C_4H_8O)_2$	961	931			224
$MoO_2Br_2(C_5H_{10}O)$	965	923	260		224
$MoO_2Br_2(C_4H_8O_2)$	969	930	265	254	224
$MoO_2Br_2(C_4H_{10}O_2)$	957	917	258		224
$MoO_2Br_2(C_{18}H_{15}PO)_2$	947	903	245		224
$MoO_2Br_2(C_{18}H_{15}AsO)_2$	955	920			224
$MoO_2Cl_2(C_{18}H_{15}PO)_2$	947	905			224
$MoO_2Cl_2(C_{18}H_{15}AsO)_2$	960	925			224
$MoO_2Br_2C_2H_3N$	960	923			224
$MoO_2Br_2(C_2H_3N)_2$	953	918			224
$MoO_2Br_2(C_3H_5N)$	962	922			224
$MoO_2Br_2(C_3H_5N)_2$	958	918			224
$MoO_2Br_2(C_4H_7N)$	967	925			224
$MoO_2Br_2(C_4H_7N)_2$	957	920			224
$MoO_2Cl_2(C_3H_5N)$	965	922			224
$MoO_2Cl_2(C_4H_7N)$	962	922			224
$MoO_2Br_2(C_5H_5N)_2$	942	909	243		224

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$MoO_2Cl_2(C_{12}H_8N_2)$	935	902			224
$MoO_2Br_2(C_{12}H_8N_2)$	933	900	244		224
$MoO_2Cl_2(C_3H_9N)_2$	965	920			224
$MoO_2Cl_2(C_4H_4N_2)_2$	948	910			224
$MoO_2Br_2(C_4H_4N_2)_2$	945	907			224
$[(MoO_2Cl_2)_2(C_{10}H_8N_2)_3]$	940	908			224
$MoO_2Cl_2(C_{10}H_8N_2)_2$	940	908			224
$[(MoO_2Cl_2)_2(C_8H_6N_2)_3]$	950	915			224
$MoO_2Cl_2(C_8H_6N_2)_2$	950	910			224
$MoO_2Cl_2(C_{20}H_{28}O_4P_2)$	952	914			225
$MoO_2Cl_2(C_{20}H_{28}O_4P_2)_2$	950	907			225
$MoO_2Cl_2(C_{22}H_{32}O_4P_2)$	956	917			225
$MoO_2(C_{10}H_9O_2)_2$	939	909			76
$MoO_2(C_{15}H_{11}O_2)_2$	931	899			76
$MoO_2(C_9H_{15}O_2)_2$	909	877			76
$MoO_2(C_5H_8NS_2)_2$	943	913			76
$MoO_2(C_{11}H_8O_3N)_2$	927	883			326
$MoO_2(C_{13}H_{10}O_2N)_2$	937	906			326
$MoO_2Br_2(C_{26}H_{24}O_2P_2)$	940	897	249		234,304
$MoO_2Cl_2(C_{26}H_{24}O_2P_2)$	945	903	325		234,304
$[MoO(O_2)_2(C_2O_4)]^{2-}$	966				327
$MoOF_4$	1030		539		54
$MoOBr_4$	998				54
MoO_2F_2	1009	987	719	692	54
MoO_2Cl_2	994	972	453	437	54
MoO_2Br_2	991	969			54
MoO_2I_2	972	950			54
$[MoO_2F_3]^-$	980	930	585	457	320
$[Mo_6O_{11}F_{24}]^{10-}$	967	927			320
$MoO_2F_2(C_{12}H_8N_2)$	945	925			312
$MoO_2F_2(C_{10}H_8N_2)$	947	918			312
$Mo_4O_8(OH)_6(C_3H_6O_2N)_2$	962	937			97
$Mo_2O_4(OH)_3(C_3H_6O_2N)_2$	957	923			97
$MoO_2(C_2H_6NS)_2$	896	874			97
$MoO_2(C_4H_8O_2NS)_2$	912	884			97
$[MoO_2(C_4H_8O_2NS)_2]^{2-}$	922	892			97

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$MoO(O_2)_2(C_3H_7ON)_2$	945				328
$MoO(O_2)_2(C_4H_9ON)(H_2O)$	965				328
$MoO(O_2)_2(C_5H_{12}ON_2)(H_2O)$	963				328
$MoO(O_2)_2(C_6H_{18}ON_3P)(H_2O)$	965				328
$MoO(O_2)_2(C_6H_{18}ON_3P)_2$	945				328
$MoO(O_2)_2(C_8H_{24}O_3N_4P_2)$	965				328
$MoO(O_2)_2(C_6H_5O_3N)$	930				328
$MoO(O_2)_2(C_5H_5ON)$	960				328
$MoO(O_2)_2(C_{18}H_{15}PO)_2$	954				328
$MoO(O_2)_2(C_{10}H_8N_2)$	940				328
$MoO(O_2)_2(C_6H_{18}ON_3P)(C_5H_5N)$	945				328
$MoO(O_2)_2(C_6H_{18}ON_3P)(C_3H_7ON)$	945				328
$MoO(O_2)_2(C_{12}H_8N_2)$	952				329
$MoO(O_2)_2(C_{18}H_{15}OAs)_2$	952				329
$MoO_2F_2H_2O$	977	932			232
$MoO_2F_2(C_2H_6OS)_2$	928	913			232
$MoO_2F_2(C_3H_7ON)$	957	905			232
$MoO_2(C_{12}H_{10}S_2P)_2$	932	901			330
$Mo_2O_7H_3(C_5H_{10}O_2NS)$	950	917			187
$Mo_2O_7H_3(C_2H_4O_2N)$	952	930			187
$Mo_2O_7H_3(C_3H_6O_2N)$	955	930			187
$Mo_2O_7H_3(C_6H_{12}O_2N)$	955	925			187
$Mo_2O_4(C_3H_6NS_2)_4$	949				65
$Mo_2O_4(C_5H_{10}NS_2)_4$	947				65
$Mo_2O_4(C_7H_{14}NS_2)_4$	950				65
$Mo_2O_4(C_9H_{18}NS_2)_4$	943				65
$[MoO_3(C_2O_4)]^-$	910	885			331
$MoO_2(C_5H_{10}O_2N)_2$	910	880			181
$MoO_2Cl_2(C_3H_9OAs)_2$	945	905	331	306	191
$MoO_2Cl_2(C_3H_9ON)_2$	946	918			191
$[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$	958				321
$[Mo_2O_5C_6H_{12}O_6]^{2-}$	923	910			322
$MoOCl_2(C_5H_5(OCH_3)$	970				333
$MoOCl_2(C_5H_5)(OC_2H_5)$	965				333
$MoOCl_2(C_5H_5)(OC_3^nH_7)$	955				333
$MoOCl_2(C_5H_5)(OC_3^iH_7)$	960				333

Compound	Mo-O_t	Mo-O_t	Mo-X	Mo-X	Reference Number
$MoOCl_2(C_5H_5)(OC_4^nH_9)$	960				333
$MoOCl_2(C_5H_5)(OC_4^iH_9)$	965				333
$MoOCl_2(C_5H_5)(OC_5^iH_{11})$	990				333
$MoOCl(C_5H_5)(OCH_3)_2$	980				333
$MoOCl(C_5H_5)(OC_2H_5)_2$	965				333
$MoOCl(C_5H_5)(OC_3^nH_7)_2$	970				333
$MoOCl(C_5H_5)(OC_3^iH_7)_2$	985				333
$MoOCl(C_5H_5)(OC_4^nH_9)_2$	965				333
$MoOCl(C_5H_5)(OC_4^iH_9)_2$	940				333
$MoOCl(C_5H_5)(OC_5H_{11})_2$	963				333

APPENDIX C

Ultraviolet and Visible Absorption Spectra of Molybdenum(V) and (VI) Compounds

Compound	Solvent Used or Solid State (S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
Molybdenum(V) Complexes			
$[Mo_2O_4(C_{10}H_{12}O_8N_2)]^{2-}$	H_2O	26.0(2.58),33.6(3.98)	308
$MoOCl(C_6H_9N)_2$	C_5H_5N	26.1(3.56),16.9(3.27)	308
$MoCl_2(OC_6H_5)_3$	C_6H_6	21.5(4.04)	308
$Mo_2O_3(C_3H_5OS_2)_4$	CH_3CN	19.8(3.98),32.3(3.94), 37.6(4.38),45.3(4.54), 50.0(4.45)	76, 217
$MoOCl_3(C_5H_8O_2)$	S.S.	14.29, 27.78	40
$MoOCl_3(C_{13}H_{10}O)_2$	C_6H_6	14.49(1.94),21.05(2.71)	40
$MoOCl_3(C_5H_5N)_2$	S.S.	13.80,20.83,26.67	40
$MoOCl(C_5H_7O_2)_2$	C_6H_6	13.51(1.70),16.81(1.92) 26.32(3.52)	40
$Mo_2O_4Cl_2(C_{10}H_8O_2N_2)_2$	S.S.	14.29,21.28	309
$Mo_2O_3Cl_4(C_{10}H_8O_2N_2)_2$	S.S.	14.49,21.74,28.99	309
$MoOCl_3(C_{10}H_8N_2)$	S.S.	13.9,18.7,23.2,30.12	80, 311
$MoOBr_3(C_{10}H_8N_2)$	S.S.	13.9,21.00, 25.6	80
$(MoOCl_2)_2(C_7H_4O_4N)_2(C_{12}H_8N_2)$	S.S.	14.28, 20.00,23.53	334
$(MoOCl_2)_2(C_6H_4O_2N)_2(C_{12}H_8N_2)$	S.S.	12.90,23.50	334
$Mo_2O_4(C_6H_4O_2N)_2$	S.S.	14.29	334
$MoOCl(C_7H_4O_4N)$	S.S.	13.30,19.04,22.00	335
$MoO_2(C_7H_4ON)(C_5H_5N)$	S.S.	13.30,25.00	335
$Mo_2O_3(C_2O_4)_2(C_6H_9ON)_2$	H_2O	27.17(3.82),32.26(3.99), 39.84(4.85)	188
$Mo_2O_3(C_2O_4)_4$	C_2H_5OH	18.42(3.72),25.00(3.92), 32.79(3.82),39.22(4.56), 41.15(4.49)	188
$Mo_2O_3(C_2O_4)_2(C_6H_4O_2N)_2$	H_2O	20.80(3.23),31.90(3.61), 37.60(3.96)	188
$Mo_2O_3(C_2O_4)_2(C_{12}H_8N_2)_2$	H_2O	27.80(3.16),36.40(4.32)	188
$[Mo_2O_4(C_3H_5O_2NS)_2]^{2-}$	H_2O	32.59(4.07)	181
$MoCl_5$	CCl_4	14.81(2.22),20.75(3.69), 38.17(3.52)	40
$MoOCl_4$	CCl_4	14.43(2.50),20.75(3.45), 37.17(3.46)	40
$MoOBr_3(C_{15}H_{11}O_2)$	CH_3CN	14.1(1.61),18.2(2.74), 21.8(sh),22.7(3.78), 27.3(sh),29.5(4.70), 35.6(sh),40(4.60)	70

Compound	Solvent Used or Solid State (S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
$MoOCl_3(C_{15}H_{11}O_2)$	CH_3CN	13.6(1.48),18.4(1.70), 19.7(1.70),22.2(2.62), 23.7(2.61),29.2(4.04), 32.8(4.18),35.5(sh), 39.4(sh)	70
$MoOCl_3(C_5HO_2F_6)$	CH_3CN	14.2(1.48),18.9(1.90), 20.3(1.90),23.7(sh), 25.4(3.41),28.5(sh), 32.2(4.04),39.7(sh), 40.5(sh),42.7(4.08)	70
$MoOCl_3(C_{10}H_6O_2F_3)$	CH_3CN	13.8(1.50),19.2(2.48), 20.5(2.30),24.1(sh), 25.1(3.60),26.1(sh), 29.9(sh),33.6(4.60), 38.2(sh)	70
$MoOCl_3(C_5H_4O_2F_3S)$	CH_3CN	13.7(1.54),18.9(2.48), 20.1(2.60),23.8(sh), 24.9(4.30),28.2(sh), 29.1(4.60),31.7(4.56)	70
$Mo_2O_3(C_5H_7O_2)_4$	CH_2Cl_2	20.62(3.79),25.00(3.32), 30.58(3.98)	217
$Mo_2O_3(C_3H_6NS_2)_4$	CH_2Cl_2	19.61(3.12),26.67(3.60)	217
$Mo_2O_3(C_5H_{10}NS_2)_4$	CH_2Cl_2	19.42(3.29),26.32(3.75), 33.00(4.26),38.50(4.78)	217, 310, 316
$Mo_2O_3(C_2H_3OS_2)_4$	C_6H_6	19.70(3.70)	217
$MoOCl_3(C_{18}H_{15}OAs)(C_3H_6O)$	CH_2Cl_2	13.90(1.76),16.70(sh), 23.60(1.71)	306
$MoOCl_3(C_3H_6O)_2$	C_3H_6O	13.80(1.31),23.30(1.40)	306
$MoOCl_3(C_{18}H_{15}OAs)_2$	CH_2Cl_2	13.60(1.71),16.00(sh), 22.60(1.58)	306
$MoOCl_3(C_2H_6OS)_2$	CH_2Cl_2	13.80(1.28),22.70(0.97)	306
$MoOCl_3(C_{18}H_{15}OP)_2$	CH_2Cl_2	13.50(1.28),22.30(1.05)	304, 306
$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$	H_2O	20.40(1.61),26.00(2.23), 32.80(3.55),38.90(3.55)	299
$Mo_2O_3Cl_4(C_{10}H_8N_2)_2$	S.S.	14.2,19.5,24.2	305
$Mo_2O_4Cl_2(C_{10}H_8N_2)_2$	S.S.	13.9,20.2,24.4	305
$MoOCl_3(C_2H_3N)_2$	CH_3CN	13.7,19.0,26.0	98
$MoOCl_3(C_4H_7N)_2$	C_3H_7CN	13.5,19.2,25.0	98
$MoOCl_3(C_4H_8O)_2$	C_4H_8O	13.4(1.60),19.05	318
$MoOCl_3(C_5H_{10}O)_2$	$C_5H_{10}O$	13.16,19.05	318
$MoOCl_3(C_4H_8S)_2$	C_4H_8S	13.16,15.15	318
$MoOCl_3(C_5H_{10}S)_2$	$C_6H_6/C_5H_{10}S$	13.16(1.15),15.38(1.04)	318
$MoOCl_3(C_4H_8O_2)$	$C_4H_8O_2$	13.07,18.35	318

Compound	Solvent Used or Solid State(S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
$MoOCl_3(C_4H_{10}O_2)$	$C_4H_{10}O_2$	13.16	318
$MoOCl_3(C_4H_8S_2)$	$C_6H_6/C_4H_8S_2$	13.51,17.54	318
$MoOCl_3(C_2H_6S)$	C_6H_6/C_2H_6S	12.99(1.30),16.39(1.26)	318
$MoOCl_3(C_4H_{10}S)$	$C_6H_6/C_4H_{10}S$	13.16(1.15),15.62(1.04)	318
$MoOCl_3(C_6H_{14}S)$	$C_6H_6/C_6H_{14}S$	13,16,15.15	318
$Mo_2O_3(C_4H_8O_2NS)_4$	S.S.	14.0,1.90,30.0,36.4,45.0	97
$Mo_2O_4(C_4H_8O_2NS)_2$	CH_3CN	34.7(3.95),36.2(3.96)	97, 181
$Mo_2O_2S_2(C_4H_8O_2NS)_2$	S.S.	22.3,27.8,36.2,45.2	97
$Mo_2O_3(C_2H_5OS)_4$	S.S.	14.6,24.0,30.0,36.4	97
$Mo_2O_4(C_2H_5OS)_2$	S.S.	30.0,35.3,45.0	97
$[Mo_2O_4(C_3H_5O_2NS)_2]^{2-}$	S.S.	29.3,35.3,45.2	97
$[Mo_2O_2S_2(C_3H_5O_2NS)_2]^{2-}$	H_2O	13.0(2.20),23.2(2.91) 28.6(3.40),36.0(3.85), 47.6(4.15)	97
$[Mo(OCH_3)_2Cl_4]^-$	CH_3NO_2	11.7(1.20),21.8(1.43)	313
$[Mo(OC_2H_5)_2Cl_4]^-$	CH_3NO_2	12.1(1.28),21.5(1.46)	313
$[MoOCl_4]^-$	CH_2Cl_2	14.6(1.36),22.7(1.28), 26.4(2.38),31.3(3.71)	313
$MoOCl_3(C_3H_2N_2)$	S.S.	13.3,20.8,26.3	315
$MoOCl_3(C_4H_4N_2)$	S.S.	13.5,21.2,27.2	315
$MoOCl_3(C_6H_8N_2)$	S.S.	13.3,20.9,26.4	315
$MoOCl_3(C_8H_4N_2)$	S.S.	13.0,21.4,26.2	315
$MoOCl_3(C_{10}H_8N_2)$	S.S.	13.7,19.6,24.3	315
$MoOCl_3(C_{10}H_8N_2)_2$	S.S.	13.1,20.8,27.0	315
$MoOCl_3(C_4H_4N_2)$	S.S.	13.9,20.1,26.5	315
$MoOCl_3(C_4H_4N_2)_2$	S.S.	13.0,19.0,25.6	315
$Mo_2O_3(C_2H_3O_2)_2(C_5H_{10}NS_2)$	S.S.	13.6,25.0,29.7,35.5,37.2	316
$Mo_2O_3(C_3H_5OS_2)_4$	S.S.	18.0,19.7,29.0,32.0	316
$MoO(C_3H_5OS_2)_2(C_5H_5N)$	S.S.	18.7,25.0,29.8,35.0,37.4	316
$Mo_2O_3(C_{12}H_{10}O_2S_2P)_4$	S.S.	18.0,20.3,23.9,30.2,37.0	316
$Mo_2O_3(C_5H_{10}O_2NS)_4$	$CHCl_3$	19.8(4.13),30.3(3.88)	181
$Mo_2O_4(C_5H_{10}O_2NS)_2$	CH_3CN	34.7(3.95),36.2(3.95)	181
$MoOBr_3(C_{18}H_{15}OP)_2$	CH_2Cl_2	13.8	304
$MoOCl_3(C_{26}H_{24}O_2P_2)$	CH_2Cl_2	13.4,22.5	304
$MoOBr_3(C_{26}H_{24}O_2P_2)$	CH_2Cl_2	13.7	304
$MoOCl_3(C_{12}H_8N_2)$	C_3H_6O	14.08(1.67),18.87(2.03), 22.99(2.37),30.31(3.73)	317
$Mo_2O_4(C_9H_4ONBr_2)(C_5H_5N)$	S.S.	13.6,25.3	336

Compound	Solvent Used Or Solid State (S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
$Mo_2O_2Cl_4(C_9H_6ON)(C_{12}H_8N_2)$	S.S.	13.9,19.23,24.06	336
$Mo_2O_4(C_{11}H_{14}O_8N_2)$	H_2O	13.80,21.00,26.6	237
$MoO(OH)(C_{44}H_{30}N_4)$	C_5H_5N	14.99(3.59),16.26(3.72), 17.09(3.63),22.42(4.77), 24.51(4.58)	319
$MoOCl(C_{44}H_{30}N_4)$	C_5H_5N	14.79(3.98),15.85(3.95), 19.84(4.64),22.32(4.43), 23.81(4.51),26.18(4.62)	319
$MoO(OOH)(C_{44}H_{30}N_4)$	C_5H_5N	15.06(3.64),15.62(3.66), 17.12(3.77),17.98(3.67), 22.47(4.77),74.33(4.62)	319
Molybdenum(VI) Complexes			
$MoO_2(C_9H_6ON)_2$	CH_2Cl_2	27.3(4.00),31.7(3.72), 40.0(4.70)	76
$MoO_2(C_6H_7O_2)_2$	CH_3CN	31.6(3.80),38.4(3.97), 48.8(4.04),52.1(4.16)	76
$MoO_2(C_{10}H_9O_2)_2$	CH_3CN	29.0(4.24),36.6(4.47), 48.2(4.68)	76
$MoO_2(C_{15}H_{11}O_2)_2$	CH3CN	26.3(4.42),35.2(4.48), 41.5(3.90),50.0(4.52), 52.1(4.69)	76
$MoO_2(C_3H_6NS_2)_2$	CH_3CN	26.5(3.46),33.3(3.88), 39.5(4.40),48.8(4.65)	76, 217
$MoO_2(C_5H_{10}NS_2)_2$	CH_3CN	26.5(3.48),33.3(4.04) 39.2(4.44),48.5(4.42)	76, 217, 310
$MoO_2(C_7H_{14}NS_2)_2$	CH_3CN	26.5(3.55),33.3(4.07), 39.2(4.44),46.1(4.24), 48.8(4.28)	76, 217
$MoO_2(C_9H_{18}NS_2)_2$	CH_3CN	26.3(3.58),33.3(4.10), 39.2(4.47),45.5(4.27), 48.8(4.36)	76, 217
$MoO_2(C_7H_6O_2N_2)_2$	C_2H_5OH	33.00(3.46)	337
$MoO_2(C_7H_5O_2NCl)_2$	C_2H_5OH	33.00(3.18)	337
$MoO_2(C_7H_5O_4N_2)_2$	C_2H_5OH	33.00(3.90)	337
$MoO_2(C_8H_8O_2)N_2)_2$	C_2H_5OH	33.00(2.09)	337
MoO_2Cl_2	$C_4H_8O_2$	27.4,38.0,44.6	225
$MoO_2Cl_2(C_{20}H_{28}O_4P_2)$	$C_2H_5OH/CHCl_3$	30.7,36.3,37.2,38.0,39.0 40.0,44.2	225
$MoO_2Cl_2(C_{20}H_{28}O_4P_2)$	$C_4H_8O_2$	27.0,36.3,37.8,38.3,40.2 46.0	225
$MoO_2Cl_2(C_{22}H_{32}O_4P_2)$	$C_4H_8O_2$	29.3,36.4,37.4,38.2,39.0 46.0	225
$MoO_2Br_2(C_4H_8O)$	C_4H_8O	29.4,33.3	224
$MoO_2Br_2(C_5H_{10}O)$	$C_5H_{10}O$	28.6,34.5,37.5,41.7,44.6	224

Compound	Solvent Used or Solid State (S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
$MoO_2Br_2(C_4H_8O_2)$	S.S.	37.5,45.2	224
$MoO_2Br_2(C_4H_{10}O_2)$	S.S.	28.3,30.2,37.7,45.0	224
$MoO_2Br_2(C_{18}H_{15}OP)_2$	CH_3CN	33.0(3.60),43.1(4.53) + phenyl bands	224
$MoO_2Br_2(C_{18}H_{15}OAs)_2$	CH_3CN	33.0(3.26),45.1(4.54) + phenyl bands	224
$MoO_2Cl_2(C_{18}H_{15}OP)_2$	CH_3CN	32.7(3.60),44.8(4.57) + phenyl bands	224
$MoO_2Cl_2(C_{18}H_{15}OAs)_2$	CH_3CN	32.8(3.11), 45.1(4.58) + phenyl bands	224
$MoO_2Br_2(C_2H_3N)$	CH_3CN	33.7,37.7	224
$MoO_2Br_2(C_2H_3N)_2$	CH_3CN	33.1(3.36),37.8(3.60), 38.6(3.59),39.5(3.53), 40.4(3.46),41.2(3.41), 45.7(3.57)	224
$MoO_2Br_2(C_3H_5N)$	C_2H_5CN	33.1,37.5	224
$MoO_2Br_2(C_4H_7N)$	C_3H_7CN	37.0	224
$MoO_2Br_2(C_5H_5N)$	S.S.	21.5,24.3,30.2,37.9,44.8	224
$MoO_2Br_2(C_{10}H_8N_2)$	S.S.	20.4,23.6,30.1,36.5,37.6 44.8	224
$MoO_2Cl_2(C_{10}H_8N_2)$	CH_3CN	31.4(3.89),36.0(3.91), 39.3(3.97),40.2(4.00), 41.3(4.04),41.8(4.08), 43.1(4.08),45.8(4.18)	224
$MoO_2Br_2(C_{12}H_8N_2)$	S.S.	20.9,25.8,38.6,47.4	224
$MoO_2Cl_2(C_{12}H_8N_2)$	CH_3CN	29.0(2.98),33.9(3.78), 35.6(3.98),36.2(4.00), 38.2(4.04),39.7(3.95), 45.7(4.23)	224
$MoO_2Cl_2(C_4H_4N_2)_2$	CH_3CN	31.6(3.23),32.3(3.28), 36.8(3.65),37.5(3.91), 38.2(3.98),38.6(3.94), 38.9(3.95),39.5(3.90), 39.8(3.86)	224
$MoO_2Br_2(C_4H_4N_2)_2$	CH_3CN	31.6(3.48),32.8(3.56), 36.9(4.04),37.6(4.20), 38.2(4.20),38.6(4.18), 38.9(4.15),39.5(4.08), 40.5(3.95)	224
$Mo_4O_8(OH)_6(C_3H_6O_2N)_2$	S.S.	37.8	97
$Mo_2O_4(OH)_3(C_3H_6O_2N)_2$	S.S.	33.0,37.4	97
$MoO_2(C_2H_6NS)_2$	$(CH_3)_2SO$	29.2(3.26),36.4(3.80), 39.8(3.86)	97
$MoO_2(C_4H_8O_2NS)_2$	C_2H_5OH	28.3(3.58),38.2(3.75), 43.5(3.99)	97

Compound	Solvent Used or Solid State (S.S.)	Peaks in kK with Log ε In Parentheses	Ref. No.
$MoO_2(C_3H_5O_2NS)_2$	S.S.	27.8, 37.0	97
$MoO_2F_2(C_2H_6OS)_2$	CH_3CN	39.3(3.42),40.3(3.43) 45.1(3.68)	232
$MoO_2F_2(C_{18}H_{15}OP)_2$	CH_3CN	36.7(3.72),37.7(3.81), 38.6(3.78),39.3(3.74), 44.5(4.47)	232
$MoO_2F_2(C_{12}H_8N_2)$	CH_3CN	36.7(4.47),44.3(4.47)	232
$MoO_2F_2(C_{10}H_8N_2)$	CH_3CN	31.1(3.86),36.1(3.88), 39.4(3.97),44.8(4.14)	232
$MoO_2(C_{12}H_{10}S_2P)_2$	CH_3OH	38.0	330
$MoO_2(C_5H_{10}NS_2)_2$	S.S.	25.0,34.2,38.7	316
$MoO_2(C_8H_{10}O_2N)_2$	H_2O	28.98	338

APPENDIX D

Magnetic Moments for Molybdenum(V) Complexes

Compound	Magnetic Moment (B.M.)	Reference Number	Compound	Magnetic Moment (B.M.)	Reference Number
$MoOCl_3$	1.62	301	$[Mo_2O_4(C_2O_4)_2(C_5H_5N)_2]^{2-}$	0.4-0.5	188
$[MoOCl_4]^-$	1.70	69,313	$[Mo_2O_3(C_2O_4)_2(C_{12}H_8N_2)_2]^{2-}$	0.4-0.5	188
$[MoOCl_5]^{2-}$	1.67	45	$MoO_2Br_2(C_{18}H_{15}OP)_2$	1.73	234
$[MoOBr_4]^-$	1.78	374	$MoO_2Br_2(C_{26}H_{24}O_2P_2)$	1.72	234
$[MoOBr_5]^{2-}$	1.70	69,375	$MoO_2Cl_2(C_{26}H_{24}O_2P_2)$	1.65	234
$MoOCl_3(C_{18}H_{25}OP)_2$	1.71	79,234	$MoOCl(C_{10}H_6O_2N)$	0.73	339
$MoOCl_3(C_2H_3N)_2$	1.70	98	$Mo_2O_4(C_{10}H_6O_2N)(C_{12}H_8N_2)$	0.20	339
$[MoOCl_4(C_2H_3N)]^-$	1.68	306	$Mo_2O_3(C_7H_6O_2N)_4$	1.27	339
$MoOCl_3(C_{10}H_8N_2)$	1.69-1.87	80,98,305, 311,340	$MoOCl(C_{10}H_6O_2N)_2$	0.73	335
			$MoOCl(C_9H_6ON)_2$	0.52	335
$MoOCl(C_9H_6ON)_2$	1.22,1.36	308,336	$MoO_2(C_{10}H_6O_2N)(C_{10}H_9N)$	0.80	335
$MoOCl_3(C_{18}H_{15}P)_2$	1.72	98	$MoOCl_2(C_{10}H_6O_2N)(C_{12}H_8N_2)_{\frac{1}{2}}$	0.21	335
$MoOCl_2(C_5H_5)$	1.74	300	$MoOCl_2(C_{10}H_6O_2N)(C_{18}H_{15}P)$	0.37	335
$Mo_2O_3Cl_4(C_{10}H_8N_2)_2$	0.84	305	$MoOCl_3(C_{12}H_8N_2)$	1.71-1.76	98,317, 340
$MoO_2O_3(C_9H_6ON)_4$	0.66	188,308			
$Mo_2O_4Cl_2(C_{10}H_8N_2)_2$	0.47,0.51	305,311	$MoOCl_3(C_3H_5N)_2$	1.72	98
$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$	0.3	299	$MoOCl_3(C_4H_7N)_2$	1.71	98
$[Mo_2O_4(C_{10}H_{12}O_8N_2)]^{2-}$	0.3	308	$MoOCl_3(C_4H_8O)_2$	1.73	318
$[Mo_2O_4Cl_4]^{2-}$	0.19	376	$MoOCl_3(C_5H_8O_2)$	1.73	318

Compound	Magnetic Moment (B.M.)	Reference Number	Compound	Magnetic Moment (B.M.)	Reference Number
$[MoOCl_3(C_5HO_2F_6)]^-$	1.75	70	$MoOCl_3(C_5H_{10}O)_2$	1.73	318
$[MoOCl_3(C_5H_4O_2SF_3)]^-$	1.87	70	$MoOCl_3(C_4H_8O_2)$	1.68	318
$[MoOCl_3(C_{10}H_6O_2F_3)]^-$	1.77	70	$MoOCl_3(C_4H_8OS)$	1.70	318
$[MoOCl_3(C_{15}H_{11}O_2)]^-$	1.63	70	$MoOCl_3(C_2H_6S)_2$	1.69	318
$[MoOBr_3(C_{15}H_{11}O_2)]^-$	1.69	70	$MoOCl_3(C_4H_{10}S)_2$	1.70	318
$Mo_2O_4Cl_2(C_{10}H_8O_2N_2)$	1.23	309	$MoOCl_3(C_4H_8S)_2$	1.75	318
$Mo_2O_3Cl_4(C_{10}H_8O_2N_2)$	1.48	309	$MoOCl_3(C_5H_{10}S)_2$	1.70	318
$[Mo_2O_3(C_2O_4)_2(C_9H_6ON)_2]^{2-}$	0.4-0.5	188	$Mo_2O_3(C_{13}H_{11}ON_4)_4$	1.08	341
$[Mo_2O_3(C_2O_4)_2(C_6H_4O_2N)_2]^{2-}$	0.4-0.5	188	$MoOCl(C_9H_4ONBr_2)$	1.02	336
$Mo_2O_4(C_9H_4ONBr_2)(C_5H_5N)_2$	0.70	336	$MoOCl(C_{44}H_{30}N_4)$	1.74	319
$[MoOCl_3(C_5H_7O_2)]^-$	1.60	342	$Mo(OOH)(C_{44}H_{30}N_4)$	1.76	319
$MoOCl_2(C_5H_5N)(C_5H_7O_2)$	1.80	342	$MoCl_6^-$	1.31	343
$MoOBr_2(C_5H_5N)(C_5H_7O_2)$	1.68	342	Magnetic Moments for Molybdenum(VI) Complexes		
$MoOBr_3(C_{10}H_8N_2)$	1.77	80	$MoO_2Cl_2(C_{18}H_{15}PO)_2^{2-}$	0.32	79
$MoOF_3(C_{12}H_8N_2)$	1.53	312	$MoO_2(C_9H_6ON)_2$	0.34	81
$Mo_2O_3F_4(C_{12}H_8N_2)$	0.4	312	$MoO_2(C_5H_7O_2)_2$	0.3	81
$[Mo(OCH_3)_2Cl_4]^-$	1.71	313	$MoO_2(C_9H_6ON)_2$	0.26	2
$[Mo(OC_2H_5)_2Cl_4]^-$	1.73	313	$MoO_2Br_2(C_{10}H_8N_2)$	0.33	80
$Mo_2O_3(H_2O_2P)_4$	0.9	314	$MoO_2Cl_2(C_{10}H_8N_2)$	0.40	80
$Mo_2O_4(H_2O_2P)_2(C_{10}H_8N_2)_2$	0.5	314			
$Mo_2O_4(H_2O_2P)_2(C_{12}H_8N_2)_2$	0.5	314			

Compound	Magnetic Moment (B.M.)	Reference Number
$MoOCl_3(C_3H_2N_2)$	1.69	315
$MoOCl_3(C_4H_4N_2)$	1.76	315
$MoOCl_3(C_6H_8N_2)$	1.70	315
$MoOCl_3(C_8H_4N_2)$	1.72	315
$MoOCl_3(C_{10}H_8N_2)$	1.86	315
$MoOCl_3(C_{10}H_8N_2)_2$	1.82	315
$MoOCl_3(C_4H_4N_2)$	1.77	315
$MoOCl_3(C_4H_4N_2)_2$	1.75	315
$MoOCl_3(C_{10}H_{16}As_2)$	1.49	66
$MoOCl_3(C_{26}H_{24}P_2)$	1.73	67
$MoO(OH)(C_{44}H_{30}N_4)$	1.75	319

APPENDIX E

Stability Measurements on Molybdenum(V) and (VI) Complexes

Ligand Used	Stoichiometry of the Complex	Stability Constant pK_f	Method Used For Measurement	Solvent Used For Measurement	Reference Number
Values for Molybdenum(V) Complexes					
8-quinolinol	1:2	12.14	Spectrophotometric	H_2O/C_3H_6O	344
8-quinolinol	1:1	16.44	Partition	$H_2O/CHCl_3$	91
8-quinolinol	1:2	30.02	Partition	$H_2O/CHCl_3$	91
5,7-dibromo-8-quinolinol	1:1	14.16	Partition	$H_2O/CHCl_3$	92
5,7-dibromo-8-quinolinol	1:2	28.32	Partition	$H_2O/CHCl_3$	92
N-benzoylphenylhydroxylamine	1:1	14.06	Partition	$H_2O/CHCl_3$	92
N-benzoylphenylhydroxylamine	1:2	28.12	Partition	$H_2O/CHCl_3$	92
acetylacetone	1:2	20.36	Partition	$H_2O/CHCl_3$	93
Triodo-8-quinolinol-5-sulphonic acid	1:1	4.87	Spectrophotometric	H_2O	345
o-phenanthroline/thiocyanate	1:1:3	5.84	Spectrophotometric	$CHCl_3$	346
Values for Molybdenum(VI) Complexes					
8-mercaptoquinoline	1:2	30.2	Partition	$H_2O/CHCl_3$	85
5-fluoro-8-mercaptoquinoline	1:2	29.6	Partition	$H_2O/CHCl_3$	347
2,2,4-trihydroxy-3-arsono-5-chloroazobenzene	1:1	6.34	Spectrophotometric	H_2O	84
Trihydroxyglutaric acid	1:1	2.15	Spectrophotometric	H_2O	348
Trihydroxyglutaric acid	1:2	3.54	Spectrophotometric	H_2O	348
8-quinolinol	1:1	17.04	Partition	$H_2O/CHCl_3$	91
8-quinolinol	1:2	33.02	Partition	$H_2O/CHCl_3$	91
acetylacetone	1:1	10.57	Partition	$H_2O/CHCl_3$	93

Ligand Used	Stoichiometry of the Complex	Stability Constant pK_f	Method Used For Measurement	Solvent Used For Measurement	Reference Number
acetylacetone	1:2	20.49	Partition	$H_2O/CHCl_3$	93
o-hydroxyacetophenoneoxime	1:2	8.97	Spectrophotometric	H_2O	349
7-iodo-8-quinolinol-5-sulphonic acid	1:1	3.42	Spectrophotometric	H_2O	350
5,7-dibromo-8-quinolinol	1:2	27.84	Partition	$H_2O/CHCl_3$	94
N-benzoylphenylhydroxylamine	1:2	26.21	Partition	$H_2O/CHCl_3$	94
N-methyliminodiacetic acid	1:1	10.38	N.M.R.	D_2O	86
ethylenediaminetetraacetic acid	2:1	19.5	N.M.R.	D_2O	235
Iminodiacetic acid	1:1	10.5	Potentiometric pH	H_2O	236
N-methyliminodiacetic acid	1:1	10.9	Potentiometric pH	H_2O	236
Nitrilotriacetic acid	1:1	11.1	Potentiometric pH	H_2O	236
Ethylenediaminetetraacetic acid	1:1	10.8	Potentiometric pH	H_2O	236
Ethylenediaminetetraacetic acid	2:1	9.7	Potentiometric pH	H_2O	236
Myricetin	1:1	4.62,4.68	Spectrophotometric	H_2O	351,352
1,2,5,8-tetrahydroxy-9,10-anthraquinone	1:1	4.11	Spectrophotometric	H_2O/C_2H_5OH	353
2-hydroxy-5-methylacetophenoneoxime	1:2	8.69	Spectrophotometric	H_2O	354
Diethylenetriaminepentaacetic acid	2:1	15.01	Potentiometric pH	H_2O	355
Triethylenetetraaminehexaacetic acid	2:1	13.81	Potentiometric pH	H_2O	355
Catechol	1:2	4.99	Potentiometric	H_2O	356
Oxalic acid	1:1	37.4	Ion exchange	H_2O	357
Malonic acid	1:1	23.1	Ion exchange	H_2O	357
Oxalic acid	1:1	6.5	Potentiometric	H_2O	87

Ligand Used	Stoichiometry of the Complex	Stability Constant pK_f	Method Used For Measurement	Solvent Used For Measurement	Reference Number
Malonic acid	1:1	7.9	Potentiometric	H_2O	87
Malonic acid	1:2	18.3	Potentiometric	H_2O	87
Succinic acid	1:1	7.7	Potentiometric	H_2O	87
Succinic acid	1:2	18.7	Potentiometric	H_2O	87
Caprohydroxamic acid	1:1	15.1	Potentiometric	H_2O	358
Caprohydroxamic acid	1:2	18.1	Potentiometric	H_2O	358
Citric acid	1:1	1.72	Ion exchange	H_2O	359
Citric acid	1:2	2.70	Ion exchange	H_2O	359
Citric acid	1:3	3.76	Ion exchange	H_2O	359
α-dithionapthoic acid	1:2	23.08	Partition	$H_2O/CHCl_3$	360
p-methoxybenzothiohydroxamic acid	1:2	10.02	Partition	$H_2O/CHCl_3$	361
Malic acid	1:1	2.03	Catalytic Change	H_2O/H_2O_2	89
Tartaric acid	1:1	3.83	Catalytic Change	H_2O/H_2O_2	89
Trihydroxyglutaric acid	1:1	8.62	Catalytic Change	H_2O/H_2O_2	89
Saccharic acid	1:1	8.36	Catalytic Change	H_2O/H_2O_2	89
Mucic acid	1:1	8.43	Catalytic Change	H_2O/H_2O_2	89
Pyrogallol	1:2	5.43	Spectrophotometric	H_2O	90
Catechol	1:2	5.1	Spectrophotometric	H_2O	90
2,3-dihydroxynaphthalene	1:2	6.30	Spectrophotometric	H_2O	90
2,3-dihydroxynaphthalene-6-sulphonic acid	1:2	6.25	Spectrophotometric	H_2O	90
Catechol-4-sulphonic acid	1:2	5.28	Spectrophotometric	H_2O	90

Ligand Used	Stoichiometry of the Complex	Stability Constant pK_f	Method Used For Measurement	Solvent Used For Measurement	Reference Number
Tiron	1:2	6.6	Spectrophotometric	H_2O	90
Pyrogallolcarboxylic acid	1:2	5.24	Spectrophotometric	H_2O	90
Gallic acid	1:2	5.36	Spectrophotometric	H_2O	90
Pyrogallol	1:2	5.64	Electrophoresis	H_2O	90
Catechol	1:2	5.35	Electrophoresis	H_2O	90
2,3-dihydroxynaphthalene	1:2	6.15	Electrophoresis	H_2O	90
2,3-dihydroxynaphthalene-6-sulphonic acid	1:2	6.43	Electrophoresis	H_2O	90
8-quinolinol-5-sulphonic acid	1:1	10.59	Kinetic Data	H_2O	88
8-quinolinol	1:1	10.36	Kinetic Data	H_2O	362
Thenoyltrifluoroacetone	1:2	4.98	Partition	H_2O/ acetophenone	363
o-methylbenzamidoxime	1:3	5.1	Spectrophotometric	H_2O/C_2H_5OH	364

APPENDIX F

Properties of Some Molybdenum Containing Enzymes

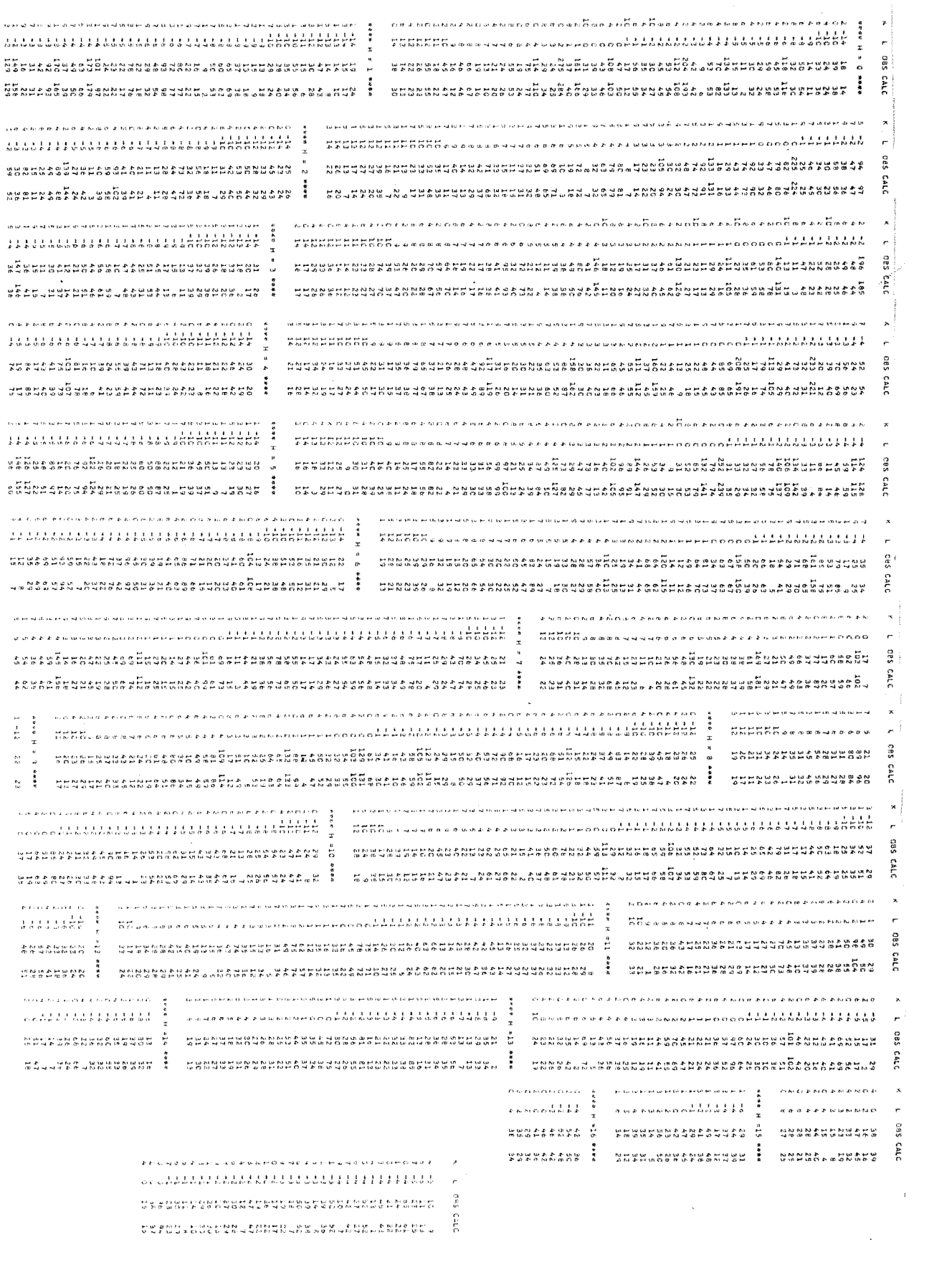
Name of Enzyme	Source	Reducing Substrate	Oxidising Substrate	Molybdenum in g.atom/ mole Mo	Flavin in g.atom/ mole Mo	Fe in g.atom/ mole Mo	Cytochrome b	MW	mole/sec/ g.atom Mo turnover	Reference Number
Nitrogenase	Clostridium Pasteurianium	Dithionite, Ferredoxin	N_2	1	-	15	-	170,000	1	365-7
Nitrogenase	Klebsiella Pneumoniae	Dithionite	N_2	1	-	17	-	220,000	1	368-9
Nitrogenase	Azotobacter Vinelandii	Dithionite	N_2	2	-	36	-	270,000	1	370
NADH Dehydrogenase	Azotobacter Vinelandii	NADH	Menadione	?	FMN(½)	1	-	?	140	371
Nitrate Reductase	Escherichia Coli	Reduced Methyl Viologen	NO_3^-	1	-	40	-	100,000,000	7,000	110
Nitrate Reductase	Neurospora Crassa	NADPH	NO_3^-	1-2	FAD	?	present	230,000	50	111
Nitrate Reductase	Asperigillus Nidulans	NADPH	NO_3^-	?	present	?	-	200,000	50	112
Sulphite Oxidase	Bovine Liver	SO_3^{2-}	O_2	2	-	-	$b_5^{(2)}$	110,000	?	372
Aldehyde oxidase	Rabbit Liver	Aldehydes	O_2	2	FAD	4	-	300,000	?	105
Xanthine Dehydrogenase	Chicken Liver	Purines, Aldehydes	NAD	2	FAD	4	-	300,000	8	106
Xanthine Dehydrogenase	Micrococcus Lactilyticus	Purines, Aldehydes	Ferredoxin	2	FAD	4	-	250,000	20	107
Xanthine Oxidase	Cow's Milk	Purines, Aldehydes	O_2	2	FAD	4	-	275,000	12	108-9

APPENDIX G

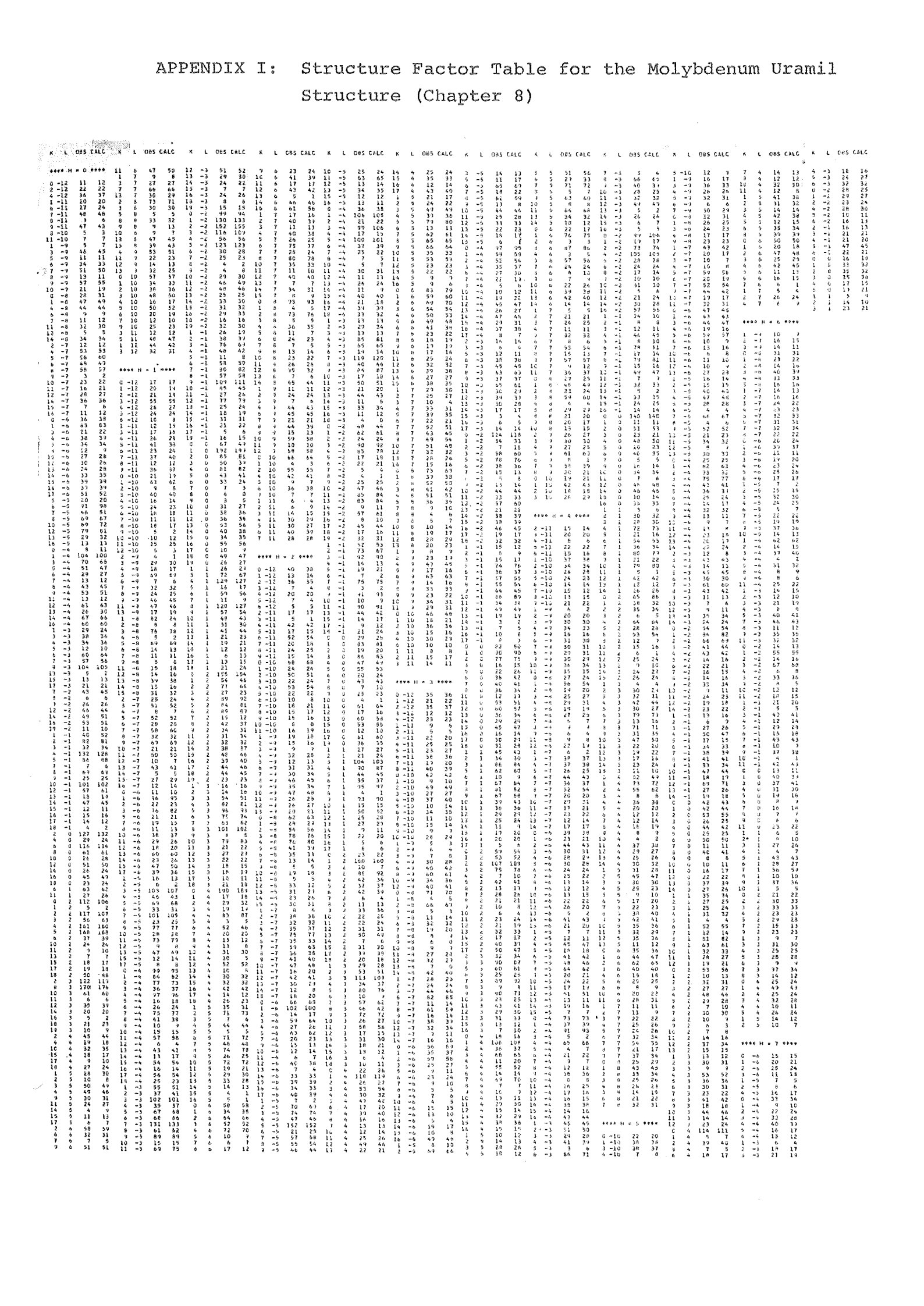
E.S.R. Signals for Some Molybdenum Containing Compounds

Compound	g	Reference
Xanthine oxidase	1.977	101
Aldehyde oxidase	1.97	101
Nitrate Reductase	1.97	101
Nitrogenase	1.97	101
$Mo(CN)_8^{3-}$	1.99	101
Mo(V)/Thioglycollic acid	1.978-2.006	101
Mo(V)/2,3-dimercaptolpropanol	2.002	101
Mo(V)/Tartaric acid	1.94	101
$[MoOCl_5]^{2-}$	1.947	101
Mo(V)/EDTA	1.936	101

APPENDIX H: Structure Factor Table for the Molybdenum Butanediol Complex (Chapter 7)



APPENDIX I: Structure Factor Table for the Molybdenum Uramil Structure (Chapter 8)



APPENDIX J: Structure Factor Table for the Molybdenum NTA Structure (Chapter 9)

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